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(OTDELENIE KHIMICHESKIKH)

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

EXPLORATORY INVESTIGATIONS IN THE FIELD OF THE CHEMISTRY AND TECHNOLOGY OF FERTILIZERS AND SALTS. I.

S. I. Volfkovich

Address at the combined meeting of the Division of Chemical Sciences of the Academy of Sciences, USSR, the Chemical Faculty of the Moscow State University and the Institute of Fertilizers and Insectofungicides, etc. on November 2, 1956

In recent years a number of scientific workers have maintained a dualistic position in relation to exploratory investigations. While recognizing the necessity for both theoretical and experimental speculation, these specialists have often considered the work of particular investigators to be unplanned, incomplete and sometimes even frivolous. Exploratory work is nevertheless an important part of nearly every creative scientific investigation; it is a stage in the course of scientific development. Without scientific exploration (whether theoretical or experimental) it would be difficult to blaze a new trail in chemical science and technology. To use the picturesque expression of A. N. Nesmeyanov, an investigator has difficulty in lifting himself onto a new plane of knowledge, or even onto a fresh step of the ladder, without preliminary exploration. The detailed study and application of already existing routes and methods essentially constitutes development in a horizontal plane. On the other hand, a new idea or a new concept, which may qualitatively alter the course of development of an industry or may only be a link in a whole chain of concepts, calls for a speculative approach (exploration) for its further development. We must therefore welcome the recent change in outlook of many scientific and technical workers who are now enthusiasts for the initiation of speculative investigations. The conservative attitude towards speculative work has resulted in the results of such work not always being considered suitable for communication or publication. To a lesser degree this scepticism has touched on the field of organic synthesis although the range of exploratory work in this field is potentially very wide. We should explain that by scientific exploratory work we do not mean shallow empiricism or shooting without a target. Whenever at all possible, experimental explorations must be preceded by a theoretical analysis and a study of the literature of the problem; in chemical technology they must also be preceded by an exploratory economic analysis. These preliminaries are important and indispensable parts of the program of exploration. During the exploratory stage of investigations touching on the interests of different sciences, it is important to come into contact with representatives of adjacent disciplines (physicists, biologists and technologists) since nowadays fortresses are attacked by different types of weapons which can be well coordinated.

After this introduction, whose objective was to clarify or justify the unusual theme of the present survey, I propose to briefly describe some exploratory investigations carried out in recent years by myself and my colleagues in the laboratory of the Ya. V. Samoilov Institute of Fertilizers and Insectofungicides and in the department of chemical technology of Moscow University.

The majority of our speculative studies were based on three fundamental ideas (or more correctly problems). The first originated from the need for a considerable increase in effective utilization of fertilizer nutrients: phosphorus, nitrogen, potash, etc. We know that on certain types of soils the soluble forms of phosphates undergo retrogression by combining with lime, sesquioxides of iron, aluminum and other soil elements to give difficultly soluble and consequently slowly assimilated (if at all) forms of plant nutrients. In other types of soils and in other climatic conditions, water-soluble fertilizers are washed out of the top layers of soil (especially sandy, solonetz, etc. soils) by irrigation and rain. The fertilizers thus enter the lower layers of soil and are removed from the sphere of action of the root system. Finally, fertilizer action may suffer in consequence of the poor mobility of

chemical compounds in soil, which hinders their absorption, diffusion, ion-exchange, etc. and creates unfavorable physicochemical conditions for the action of the root system due to unsuitability of the concentration and pH of the nutrient solution and to other factors.

Some chemical compounds are not employed in agriculture due to their inadequate stability at the normal temperature. Examples of these are ammonium carbonate and compounds containing elements undesirable for certain plants, e. g. , the chlorine ion in potassium chloride and ammonium chloride. Here we are not referring to the losses associated with unfavorable conditions of storage of fertilizers and of their distribution in the soil. Some of these defects are eliminated by granulation and conditioning of the fertilizers by various additives. The ideal fertilizers would therefore be those that supply nutrient direct to the plant (without risk of being washed out of the soil) and would supply nutrient to the plant at a rate appropriate to the soil and the physiological and climatic conditions.

In recent years physiologists and agricultural chemists have clarified some problems of the metabolism and the kinetics of assimilation of nutrients by plants with the help of isotopes of phosphorus, calcium, nitrogen and carbon. Progress has also been made through the application of colloid chemistry and methods of x-ray, chromatographic and spectral analysis. The problem is naturally a complex one, calling for much theoretical and methodological study in which chemists must collaborate with agricultural chemists, and its solution necessitates lengthy exploratory work in a variety of directions.

The second important problem arises from the circumstance that the chemistry of compounds of phosphorus, sulfur, arsenic and a number of other elements of great significance in agriculture and chemical industry has only developed over a narrow section and predominantly from the technological aspect. Hence, the limited number of salts and other inorganic compounds available to industry and the "large blank spaces on the map" of compounds of these elements. Again, little study has been made of a number of physicochemical properties of known compounds, for example, the industrially important susceptibility to polymerization and the properties of polymer-oxides and other compounds of phosphorus, sulfur, arsenic, selenium, etc. Little attention has been paid to the structure and thermodynamics of these compounds and their susceptibility to complex formation in spite of the great significance of such properties not only for fertilizers but also for new types of phosphate glasses, for water purification, for plasticizers, etc.

The third important task, coming within the field of chemical technology, is the search for simpler and more efficient methods of production and the development of a methodological basis and classification of processes and equipment that would facilitate the application of experience in one field to other fields. Such a methodology would shorten the period of pilot and semi-technical investigations of new processes for industry. A final objective of this group of investigations, which involves generalization of the existing great mass of experimental and quantitative data for a series of typical industrial processes, is the derivation of mathematical relations on the basis of similarity theory and miniature-scale operation in order to save time and materials when carrying out experiments on the large scale.

In the present brief survey I am limiting myself to exploratory work on phosphates, fluorides, nitrates and some new forms of salts and fertilizers, as well as to processes of chemical technology and to problems simultaneously involving chemistry, agriculture and soil science.

It will be convenient to arrange the various exploratory studies in three groups: 1) new products; 2) new methods of production; 3) development of theoretical concepts and derivation of mathematical laws. In some researches the search for new products is linked to new methods for their manufacture. In isolated cases the development of theoretical concepts and the derivation of mathematical laws (correlating various parameters) led to the discovery of new properties of products and of new manufacturing methods.

New Products

Below we list in chronological order the products that we investigated, their properties and methods of production. These products have not yet been made on the large scale; methods for their manufacture have not been sufficiently developed, but they are of potential interest. Such products are: metaphosphates of ammonium, potassium and magnesium; phosphamino compounds; phosphates of urea and melamine; magnesium ammonium phosphate, zinc ammonium phosphate and iron ammonium phosphate; slowly soluble (in the soil) nitrogen, potash

and complex fertilizers; and chlorides and oxychlorides of phosphorus*; fluorides and silicofluorides of magnesium, zinc, barium, etc.; organic compounds for improvement of soil structure (conditioners): "hydracryl," ammonium lignosulfonates, urea derivatives and other compounds.

Exploratory experiments on the methods of preparation of ammonium metaphosphate (NH_4PO_3) were carried out with the aim of obtaining more concentrated nitrophosphate fertilizers containing up to 73.2% P_2O_5 and 17.5% NH_3. Our experiments showed that this salt can be obtained in various polymeric forms with differing solubilities and consequently with differing rates of assimilation of the nitrogen and phosphorus by plants. Some polymeric forms of ammonium metaphosphate can also find application as insoluble fire-proofing and water-softening media. Ammonium metaphosphate is apparently the only simple ammonium salt that is insoluble in water; it can therefore be used as a fire-proofing material for treatment of wood, fibers, plastic masses and the like. Due to the diverse polymeric forms, some of which differ also in content of crystal water, ammonium metaphosphates possess diverse physicochemical properties and are of considerable theoretical interest.

The following polymers of ammonium metaphosphate are encountered in the literature: NH_4PO_3; $(NH_4PO_3)_2$; $(NH_4PO_3)_3$; $(NH_4PO_3)_4$; $(NH_4PO_3)_4 \cdot 8H_2O$; $(NH_4PO_3)_5$; $(NH_4PO_3)_6$; $(NH_4PO_3)_{10}$; $NH_4PO_3 \cdot 3H_2O$ (β-ammonium metaphosphate); $(NH_4PO_3)_{10} \cdot 12H_2O$. Although data are given in the literature for the solubility, electrical conductivity, viscosity and other properties of a number of these ammonium metaphosphates, some of the measurements were made by obsolete methods and are incomplete or difficultly comparable. The preparative details are also not trustworthy in a series of investigations. The majority of the methods of production of the above salts do not comply with modern technological requirements from the economic aspect. It was therefore necessary to develop an efficient method of production of a modification of ammonium metaphosphate that would be sufficiently soluble or mobile in soil. Current ideas about the structure of metaphosphates (Treadwell, Pascal, Thilo, Khodakov and others) are based on their susceptibility to complex formation and on the release of water on condensation of phosphoric acids. This process leads to coordinative saturation of the phosphorus with formation of a cyclic structure.

Thirty years ago, E. V. Britske and A. P. Dunaev proposed to prepare ammonium metaphosphate by reacting NH_3 with the P_2O_5 obtained by oxidation of the gases evolved from the furnace for sublimation of phosphorus. This method was investigated in the laboratory, the salt being precipitated with an electrostatic filter. The pyro- and ortho-salts were found to be formed together with metaphosphate in dependence on the temperature, the moisture content of the gases, and other conditions. The investigation was not pursued further due to the relatively high cost of P_2O_5 and the difficulty of obtaining a pure salt with a specific composition and structure. Only recently has this process again attracted the attention of the American chemical industry which has tried it out on a semi-technical plant.

In view of the defects of this process, V. V. Urusov and Z. G. Kulagina (with participation of the present writer) studied two other methods of manufacture of the metaphosphate: 1) reaction of diammonium phosphate with phosphorus pentoxide and ammonia at increased pressure (by a method similar to that described in a German patent); 2) dehydration of ammonium orthophosphate by heating in a medium of gaseous ammonia as proposed by V. V. Urusov.

The first method may be represented by the equations:

$$(NH_4)_2HPO_4 \rightarrow NH_4PO_3 + NH_3 + H_2O;$$
$$P_2O_5 + 2NH_3 + H_2O = 2NH_4PO_3$$

or by the over-all equation:

$$(NH_4)_2HPO_4 + P_2O_5 + NH_3 = 3NH_4PO_3.$$

* Up to recently these compounds were made from elemental phosphorus and chlorine; in the present case we are dealing with products of chlorination of natural phosphates under reductive or oxidative conditions (further details in Communication II).

Experiments in which the reactants were stirred in an autoclave under a pressure of 0.5 to 10 atmos, in the temperature range of 70-200°, showed that this method can yield both crystalline and glassy products close to the theoretical composition of anhydrous ammonium metaphosphate. A temperature of about 250° at atmospheric pressure is necessary for formation of water-insoluble polymeric forms. Production of an ammonium metaphosphate with maximum solubility in water and in citric acid solution was achieved at a temperature of 70° and a pressure of 2 atmos. High activity of the preparations was established in agrochemical tests.

The method proposed by Urusov consisted in the thermal breakdown of mono- or diammonium phosphate to metaphosphate in a medium of gaseous ammonia in accordance with the equation:

$$NH_4H_2PO_4 - H_2O = NH_4PO_3$$

or

$$(NH_4)_2HPO_4 - NH_3 - H_2O = NH_4PO_3.$$

The solid salt was heated in a stream of ammonia at 240- 350°. These experiments showed that an ammonium metaphosphate containing 17.5% NH_3 and 72% P_2O_5 could thus be obtained, i. e., close to the theoretical composition. Depending upon the temperature and duration of heating of the salt, the product may contain more (up to 94-97%) or less (down to 6-7%) water-soluble or citrate-soluble P_2O_5, while under certain conditions all of the salt passes into the substantially insoluble state. The content of water-soluble P_2O_5 decreases with increasing duration of heating. The hygroscopicity of ammonium metaphosphate corresponds to 3-4 points on the Pestov scale.* Different forms of the salt were subjected to x-ray and thermographic examination and their characteristic features were determined. Plant trials at the D.N. Pryanishnikov Agrochemical Experiment Station (Dolgoprud) showed that the forms of metaphosphate under test are not inferior in activity to ammonium orthophosphates, and that in the majority of cases the water-soluble specimens had no advantages over those insoluble in water. On techno-commercial grounds the second method has a number of advantages over the methods described in the literature (the relatively expensive phosphorus pentoxide is not required and increased pressure is also unnecessary). A still unsolved problem is the design of the plant for heating of the salt in a stream of gaseous ammonia which needs further development and testing on the experimental scale. The degree of polymerization of the salt in dependence on the physicochemical conditions of its preparation also calls for more detailed investigation. This thermal method merits further technological development.

Potassium metaphosphate (KPO_3) is of interest as being the most concentrated potassium phosphate fertilizer (60% P_2O_5 and 40% K_2O), especially in connection with the fertilizing of a series of citrus and other fruit crops, tobacco and flowers. Depending upon the temperature and duration of heating of the original acid potassium orthophosphate, upon the subsequent thermal treatment (rapid or slow cooling) and upon the presence of impurities (oxides of iron and aluminum, chlorides and sulfates of sodium, potassium, calcium, etc.), we can obtain potassium metaphosphate with greater or lesser solubility in water, in citric acid solution or in ammonium citrate solution, or a product entirely insoluble in these reagents. V. V. Urusov and A. S. Lachkova established by the thermographic method a relation between the content of phosphates of various solubilities and the temperature. The experiments of E. E. Zusser (Institute of Fertilizers and Insectofungicides) showed that the presence of over 3% Fe_2O_3 or Al_2O_3 in potassium metaphosphate rendered the latter water-soluble. Zusser proposed a method of manufacture of a fertilizer containing potassium metaphosphate by reacting natural phosphate with potassium chloride and sulfuric acid in a superphosphate den or in a drying drum with heating of the product to 300-400°.

In our laboratory experiments with Zh. V. Kirillova, and more recently with T. A. Banshchikova (Moscow State University), we tested the effect on the solubility of potassium metaphosphate of small additions of NaCl, KCl, $CaCl_2$, $MgCl_2$, sulfates and silicates, as well as of Al_2O_3 and Fe_2O_3. Metaphosphates were prepared by heating KH_2PO_4 at temperatures of 320 to 960°, various polymers being thus obtained. Specimens of metaphosphate prepared at 320° contained 21% P_2O_5 in the water-soluble form and 62% in the citrate-soluble form. A small admixture of magnesium chloride completely converted the P_2O_5 to the water-soluble form; admixtures of chlorides

* N. E. Pestov, Physicochemical Properties of Granular and Pulverized Chemical Products (Acad. Sci. USSR Press, 1947).

of potassium, sodium and other elements did not have this effect on the water solubility of the product; they dissolved to approximately the same extent in ammonium citrate solution. Specimens of potassium metaphosphate prepared at 900° were converted entirely to the water-soluble form on addition of 0.5% of iron oxide. The same effect was produced by addition of Al_2O_3, NaCl, $MgCl_2$ and $CaCl_2$ when incorporated in the proportion of 3%. The heating curves of KH_2PO_4 in admixture with the above additives (recorded with the help of N. S. Kurnakov's pyrometer) revealed supplementary exothermic effects which are evidently associated with formation of new chemical compounds. The water solubility of metaphosphate was also favorably influenced by the presence in it of residual water retained due to incomplete dehydration of the original ortho-salt.

The experiments thus demonstrate the value of a detailed study of the influence of small amounts of water and other salts on the solubility of potassium metaphosphate. A similar investigation is now in progress on the behavior of magnesium metaphosphate in presence of additives (N. A. Sokolov). A first series of experiments gave results similar to those obtained with potassium metaphosphate. Magnesium chloride and residual water were the most effective agents for conversion of P_2O_5 into the water-soluble form.

We pointed out above that in recent years agrochemists have been concerned with the problem of producing fertilizers that would feed plants and not be fixed in the soil. Compounds of amido- and imido-substituted phosphoric acids were synthesized for this purpose by T. I. Sokolova at the Scientific Research Institute for Fertilizers and Insectofungicides. Some of these compounds possessed the property of not being absorbed by the soil complex; in the opinion of Prof. A. V. Sokolov (Agrochemical Division of the Scientific Research Institute for Fertilizers and Insectofungicides) they are of interest as a new form of phosphate fertilizer differing fundamentally from the fertilizers in current use.

In the search for a simple and convenient method of production of amides of phosphoric acids, I. V. Olkhova (in consultation with A. M. Malets) carried out a number of experiments at the Moscow State University, starting from gaseous ammonia and phosphorus pentoxide which were heated at about 500° (the reaction is exothermic). In this manner they synthesized compounds whose compositions were close to those of triortho- and tripyrophosphamic acids, $(NH_2)_3PO_4$ and $(NH_2)_3HP_2O_4$. They also obtained a substance approximating to a mixture of dipyrophosphamic acids. A product corresponding to triorthophosphamic acid contained 44% nitrogen and 31% phosphorus; it has good solubility in water and acids, and in solution the greater part of it changes into ammonium phosphate. It is insoluble in the common organic solvents. This investigation merits development on the technological scale; a detailed study should also be made of the physicochemical and agrochemical properties of this group of compounds; they are potentially interesting not only as fertilizers but also as fire-proofing agents and as components of substrates for fermentation processes and for baking.

In collaboration with E. E. Zusser and R. E. Remen we synthesized melamine ortho-, pyro- and metaphosphates* as thermal insulants and as water-insoluble preparations for impregnation of fabrics, wood and plastic masses. Three methods of preparation of melamine metaphosphate were tested. The simplest and most economical of these was the suspension method which involved reaction of melamine with metaphosphoric acid, both reactants being in aqueous suspension. By using the solid reactants in place of their very weak solutions (due to poor solubility), the size of the equipment is considerably reduced, the dissolving operations are eliminated and the periods for decantation, filtration and washing of the products are cut down.**

Two methods of preparation of melamine pyrophosphate were studied and gave products of equally good quality: a) from melamine and orthophosphoric acid followed by heating of the melamine orthophosphate to 250-260°; b) from solutions of melamine and sodium pyrophosphate followed by treatment of the mixture with hydrochloric or nitric acid. The most water-soluble of the three melamine phosphates is the pyrophosphate. The most hygroscopic is melamine metaphosphate and the least hygroscopic is the pyrophosphate. The structure of all of these compounds was studied. The methods of preparation of melamine pyro- and metaphosphates should be tested under semi-technical conditions.

Another fire-proofing agent and complex fertilizer that merits attention is magnesium ammonium phosphate $MgNH_4PO_4$. Several attempts have been made in the last 2 or 3 decades to use magnesium ammonium phosphate as a multinutrient fertilizer containing three nutrient elements (phosphorus, nitrogen and magnesium). These attempts have, however, not met with success in spite of the extremely favorable evaluation of this fertilizer by

* S. I. Vol'kovich, E. E. Zusser and R. E. Remen, Melamine phosphates, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 571.

** Employment of suspended reactants is also of interest in connection with manufacture of a series of other compounds.

the agricultural experimental stations. This lack of success is due to the instability of $MgNH_4PO_4 \cdot 6H_2O$ during storage. Even at 30-50° this salt loses an appreciable amount of ammonia. Nor has magnesium ammonium phosphate found practical application as a fire-proofing agent although it might have been expected to be effective in cases where an insoluble salt containing phosphoric acid and ammonia is required. Most of the flame-proofing agents containing these highly effective components are soluble in water and therefore unsuitable for introduction into organic materials which are exposed to the action of water (wood, a number of plastic masses, building materials, etc.).

Study of the equilibrium systems $MgO-NH_3-P_2O_5-H_2O$ and thermographic investigations indicate the possibility of preparation under specific conditions of a magnesium ammonium phosphate containing not six molecules but only one molecule of water of crystallization, which does not decompose when stored at temperatures up to 230° and which possesses other advantages as a fertilizer and flame-proofing agent over the hexahydrate. The monohydrate is hardly hygroscopic whereas the hexahydrate is capable of taking up a large amount of moisture from the air. Due to the lower content of crystal water the monohydrate has a higher concentration of useful components: it contains 45.7% P_2O_5, 10.9% NH_3 and 25.9% MgO, whereas the hexahydrate contains 28.9% P_2O_5, 6.9% NH_3 and 17% MgO. According to our investigations,* the latter is insoluble in water but readily soluble in ammonium citrate solution and 2% citric acid solution, and it is a valuable fertilizer for a series of agricultural crops and soils.

Experiments on the application of magnesium ammonium phosphate as a flame-proofing agent in some combustible plastic masses confirmed the effectiveness of this salt. Thermograms plotted with the Kurnakov pyrometer show that $MgNH_4PO_4 \cdot H_2O$ has three endothermic effects when heated to 370°: at 92-106° (loss of water); at 244-273° (loss of ammonia); and at 310-314° (loss of ammonia). Part of the ammonia remains in the product even at 370°. The ammonia losses do not exceed 0.03% when air is passed over the salt for 5 hours at 105°.

In view of the above-mentioned advantages of the monohydrate over the hexahydrate of magnesium ammonium phosphate, the authors developed a method for its manufacture. The starting components are phosphoric acid, ammonia and a magnesium salt (chloride or carbonate) or magnesium hydroxide:

$$H_3PO_4 + NH_3 + MgO = MgNH_4PO_4H_2O.$$

The method that we developed in collaboration with R. E. Remen differs from those previously described in that the components are reacted and the salt is precipitated in boiling solutions. This method was used at the experimental plant of the Institute for Fertilizers and Insectofungicides for preparation of several batches of the monohydrate which underwent successful tests as fire-proofing agent (for linoleum) and as fertilizer. The investigations justify the application of the process on the semi-technical scale in order to obtain techno-commercial data during continuous operation. R. E. Remen has also developed processes for manufacture of zinc ammonium phosphate and iron ammonium phosphate which have potential value in various fields.

In the acidic and thermal processing of natural phosphates to give fertilizers and other products, a considerable amount of fluorine is evolved, mainly in the form of gaseous silicon tetrafluoride or fluosilicates. Apart from rendering innocuous and utilizing the fluorine, usually present in phosphorites and apatites to the extent of 2.5-3.2%, the fertilizer and salts industry is faced with the problem of widening the range of fluorides and of converting fluosilicates into fluorides. Laboratory studies have been made of methods of production of a number of fluorides and fluosilicates, including those of magnesium, calcium, zinc, and ammonium.

A study is now under way by the method of physicochemical analysis of the possibility of transformation of silicon tetrafluoride into hydrogen fluoride by the method of hydrolysis with steam according to the equation:

$$SiF_4 + 2H_2O = 4HF + SiO_2.$$

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* S. I. Volfkovich and R. E. Remen, Ammonium Phosphates of Magnesium, Zinc and Iron, Paper in the symposium on applied chemistry dedicated to Acad. E. V. Britske, Acad. Sci. USSR Press, 1955, pp. 143-174.

Satisfactory technical solution of this problem would considerably increase the efficiency of utilization of the waste fluorine gases of phosphate fertilizer plants and would open up new routes to the manufacture of fluorine compounds.

Apart from inorganic fertilizers our attention has been directed in recent years to organic products for improving the structure of soils (sometimes known as structure-forming fertilizers or soil-conditioners). Such substances must be able to improve the state of aggregation of soil, increase its adsorptive and chemosorptive capacity, facilitate water uptake, and retain the nutritive elements in the soil and release them to the plant. Many investigators in a number of countries have been working on these problems for the past 10-20 years. These studies are based on the one hand, on modern ideas of soil colloids and ion-exchange complexes advanced by K. K. Gedroits, E. N. Gapon and others, and on the other hand, on the achievements of the chemistry of high-molecular compounds.

Organic substances play many parts in soils: they act as nutrients and soil modifiers, as growth stimulators and as a substrate for the growth of microorganisms. Some soil specialists attach very great importance to the development of good soil conditioners. A number of organic compounds have been put forward for this purpose in other countries ("krilium," "poliak"), the sodium salt of polyacrylonitrile, and many others. For some years past the problem has been studied in the USSR at the physico-agronomic institute of VASKhNIL (Lenin All-Union Academy of Agricultural Sciences).

We started exploratory work in this direction at Moscow University some years ago in collaboration with V. K. Kuskov and R. M. Fedorovich in association with the agrochemical division of the Scientific Research Institute for Fertilizers and Insectofungicides (Prof. F. V. Turchin). The first exploratory studies involved the synthesis and testing of various organic compounds obtainable from readily accessible and comparatively cheap raw materials. We tested about 25 such compounds as conditioners; they were first tested for their effect on the aggregation and swelling of soils, for resistance to leaching and their hygroscopicity; later their value in pot tests was assessed. They were tested in comparison with products of hydrolysis of polyacrylonitrile, salts of humic acids and products of condensation of glycerol with phthalic anhydride. Later tests were carried out in comparison with petroleum products, polymeric products of reaction of urea, formaldehyde and phosphates (we named these "carbamiforms"), ammonium and calcium lignosulfonates, products of treatment of lignite, etc.

Some of these tested products showed great activity in pot tests and they consequently require much further study from the physicochemical, agrochemical and technological aspects. Products of reaction of urea and formaldehyde with phosphates may be of potential interest. The same is true of other urea-formaldehyde derivatives. Depending upon the ratios of reactants and the physicochemical conditions, the latter may contain 30-38% nitrogen, may have a wide range of solubility in water and ammonium citrate solution, or may be substantially insoluble. This opens up the possibility of making fertilizers with specified rates of release of nitrogen to plants in dependence on the type of soil and the water supply (experiments of V. A. Afanasyeva, N. L. Solomonova, R. S. Sarro and others). These investigations are being continued at the Moscow State University.*

* Exploratory work on new methods of production of fertilizers and salts, as well as on the development of theoretical ideas, are discussed by the author in the next issue of Bull. Acad. Sci. USSR, Div. Chem. Sci. (1957, No. 7).

THE ADSORPTIVE PROPERTIES OF CARBONACEOUS ADSORBENTS

I. ANALYSIS OF PREVIOUSLY OBTAINED EXPERIMENTAL DATA

M. M. Dubinin, E. D. Zaverina and D. P. Timofeev

Timofeev [1] has carried out systematic measurements of the isotherms of adsorption of various vapors by active carbons. Timofeev's experiments made possible the experimental evaluation for many vapors of the coefficients of affinity of the characteristic curves of the potential theory of adsorption [1, 2]; they also served to confirm the approximate concepts of the relation between adsorbability and the physical properties of vapors [1-3].

Fundamental problems of the potential theory of adsorption of gases and vapors were attacked at the same time [4-7]. This work led to the establishment of a correlation between the porous structure of a carbon adsorbent and the equation of the characteristic curve, and an attempt was made to establish a theoretical basis for this relationship. Further development of the concept of structural types of carbonaceous adsorbents was thus achieved and equations were derived for the adsorption isotherms for adsorbents with specific types of structures. One of these equations was used by Timofeev in a theoretical analysis of the relation between adsorbability of vapors and their physical properties [1, 2].

In the initial stage of these researches it was not possible to immediately employ the most efficient methods of treatment and analysis of the measured adsorption isotherms. In particular, the coefficient of affinity of the characteristic curves was determined graphically. The immediate problem was solved in this manner, but the complete correspondence between theory and experiment could not be established.

In the present paper the experimental data of Timofeev are subjected to more complete examination and analysis in order to confirm the fundamental principles of the potential theory of adsorption and to provide a basis for a number of implications of that theory.

Method of Treatment of the Experimental Data

The equation of the isotherm of adsorption of a given vapor has the gollowing form [5] for an active carbon with fine micropores in which the adsorption potentials of the dispersion forces are much increased, i. e., for an active carbon of the first structural type:

$$a = \frac{W_0}{v} e^{-B\frac{T^2}{\beta^2}\lg(p_s/p)^2} \qquad (1)$$

where W_0 is the limiting volume of the adsorption space, v is the volume of one millimole of adsorbate in the liquid state, β is the affinity coefficient of the characteristic curve relative to the characteristic curve for a standard vapor ($\beta = 1$), B is the constant of the equation which is determined, like the limiting volume of the adsorption space W_0, from the adsorption isotherm of the standard vapor.

To save space we shall denote the relative vapor pressure by h:

$$h = p/p_s \qquad (2)$$

and the logarithm* of the reciprocal of the relative pressure by H:

$$H = \lg p_s/p. \tag{3}$$

The equation of the adsorption isotherm (1) in the linear form may be written:

$$\lg a = C - DH^2, \tag{4}$$

where

$$C = \lg \frac{W_0}{v} \tag{5}$$

and

$$D = 0.434B\frac{T^2}{\beta^2}. \tag{6}$$

For the standard vapor (benzene in our experiments) $\beta = 1$. Equation (6) then becomes:

$$D_0 = 0.434BT_0^2; \tag{7}$$

and from (6) and (7) we obtain:

$$\beta = \frac{T}{T_0}\sqrt{\frac{D_0}{D}}. \tag{8}$$

The extent to which Eq. (1) fits the experimental data can be judged by plotting log a against H^2. The resultant graph also enables us to evaluate the range of relative pressures in which Eq. (1) satisfactorily expresses the results of experiments. From the parameters of the straight lines C and D determined from the graph for the standard vapor on the basis of Eqs. (5) and (7), we can calculate the constants of the equation of the adsorption isotherm, W_0 and B. The experimentally determined adsorption isotherms for other vapors enable us to find, using Eqs. (5) and (8), the limiting volumes of the adsorption space and the coefficients of affinity β for other vapors, taking into consideration the range of relative pressures for each vapor over which the equation of the adsorption isotherm fits the experimental data .

Thus, the graphical treatment of the experimental data and the application of the equation of the adsorption isotherm in the linear form (4) enables us to directly check the conformity of the equation to the experimental data and to determine the range of relative pressures h in which the equation is applicable. Moreover, from the parameters of the straight-line plot for the standard vapor, we find the constants of the equation W_0 and B, while from the parameters of the straight-line plot for other vapors we find the values of W_0 and β corresponding to the experimental data for each vapor. Apart from the very fact of applicability of the equation of the adsorption isotherm in the evaluated range of equilibrium relative pressures, an important check on the validity of the theory can be obtained by considering the values of W_0 and β for various vapors and adsorbent carbons.

For active carbons of the first structural type, adsorption takes place in the space of the adsorbent bounded by the walls of the micropores. This is substantially true if the limiting porosity of the carbon is not too highly developed. In consequence, the micropores are filled during the primary adsorption process as a result of contact of the adsorption layers at the opposing walls of the pores. The limiting volumes of the adsorption system must then be substantially the same for different vapors and must coincide with the volume of the micropores of the active carbon. This is one of the fundamental principles of the theory which is being subjected to experimental verification.

A reliable experimental determination of the coefficients of affinity has a fundamental value since these coefficients directly express the ratio of the adsorption potentials or the energies of adsorption of the vapor under consideration and the standard vapor. To a sufficiently close approximation the coefficient of affinity of each

* [In this paper 'lg' ≡ 'log' – Editor's note.]

TABLE 1

Constants of the Equation of the Adsorption Isotherms and Coefficients of Affinity of the Characteristic Curves

Vapor	AG carbon					KAU carbon					β (mean)
	C	$D\cdot10^3$	range of applicability of h	W_0 in cm^3/g	β	C	$D\cdot10^3$	range of applicability of h	W_0 in cm^3/g	β	
Benzene	0.615	3.92	$3\cdot10^{-5}$—$4\cdot10^{-2}$	0.366	1.00	0.740	3.73	$3\cdot10^{-5}$—$1\cdot10^{-1}$	0.489	1.00	1.00
Cyclohexane	0.525	3.52	$1\cdot10^{-5}$—$4\cdot10^{-2}$	0.349	1.05	0.660	3.47	$3\cdot10^{-5}$—$1.5\cdot10^{-1}$	0.493	1.04	1.045
Toluene	0.532	2.30	$1\cdot10^{-5}$—$4\cdot10^{-2}$	0.360	1.30	0.645	2.01	$1\cdot10^{-5}$—$4\cdot10^{-2}$	0.469	1.36	1.33
Propane	0.660	7.67	$7\cdot10^{4-}$—$1\cdot10^{-1}$	0.402	0.71	0.765	7.07	$3.4\cdot10^{-4}$—$1\cdot10^{-1}$	0.511	0.72	0.715
n-Butane	0.588	5.15	$1.3\cdot10^{-4}$—$1\cdot10^{-1}$	0.380	0.87	0.720	5.22	$1.3\cdot10^{-4}$—$1.5\cdot10^{-1}$	0.515	0.86	0.865
n-Pentane	0.515	3.22	$2\cdot10^{-5}$—$4\cdot10^{-2}$	0.362	1.10	0.647	3.32	$2\cdot10^{-5}$—$1\cdot10^{-1}$	0.512	1.06	1.08
n-Hexane	0.460	2.30	$1\cdot10^{-5}$—$2\cdot10^{-2}$	0.374	1.30	0.580	2.23	$1\cdot10^{-5}$—$3\cdot10^{-2}$	0.494	1.29	1.295
n-Heptane	0.417	1.87	$2\cdot10^{-6}$—$2\cdot10^{-2}$	0.384	1.44	0.535	1.70	$2\cdot10^{-6}$—$4\cdot10^{-2}$	0.505	1.48	1.46
Chloroform	0.655	5.02	$3\cdot10^{-5}$—$4\cdot10^{-2}$	0.362	0.88	0.790	5.16	$1\cdot10^{-5}$—$1\cdot10^{-1}$	0.494	0.85	0.865
Carbon tetrachloride	0.610	4.28	$1\cdot10^{-5}$—$1\cdot10^{-1}$	0.392	0.96	—	—	—	—	—	0.96
Ethyl chloride	0.710	7.40	$2.5\cdot10^{-4}$—$1.3\cdot10^{-1}$	0.363	0.73	0.840	7.72	$2.5\cdot10^{-4}$—$1.5\cdot10^{-1}$	0.490	0.69	0.71
Methyl bromide	0.815	11.8	$7\cdot10^{-4}$—$1\cdot10^{-1}$	0.359	0.58	0.955	12.2	$7\cdot10^{-4}$—$1.5\cdot10^{-1}$	0.495	0.55	0.565

vapor ought not to be influenced by the type of porous structure of the adsorbent carbon. This consequence of the theory can likewise be tested experimentally.

Results Obtained

Timofeev measured the sorption isotherms of 16 vapors at 20 and 0° on two specimens of active carbons [1, 3]. These carbons were prepared under laboratory conditions by activation with carbon dioxide and steam at 900-950° until a burn-off of about 60% of the carbonized granules from highly dispersed anthracite powder containing wood tar as binder (AG carbon) and from grains of carbonized walnut shell (KAU carbon). Samples of AG and KAU carbons (grain size 0.75-1.25 mm) were twice washed in platinum beakers by treatment with hydrochloric and hydrofluoric acids; the products were finally washed with distilled water, dried and heated in vacuum at 450°.

Timofeev's investigations were carried out prior to the development of the concepts of structural types of active carbons [5]. From the modern standpoint, therefore, the above procedure for activation of carbons was characterized by excessive burn-off, as reflected in the considerable narrowing of the range of applicability of the equation of the adsorption isotherm (1) from the side of high relative pressures.

Twelve adsorption isotherms of vapors of different substances at 20° were selected for detailed treatment and analysis. We excluded adsorption isotherms of vapors of water, methanol, formic and acetic acids because of the complicated mechanism of adsorption which called for special treatment.

For the different vapors and active carbons, Table 1 gives constants C and D of the equation of the isotherm of adsorption (1) in the linear form (4), the ranges of relative pressures in which the equation satisfies the experimental data, and the calculated values of the limiting volumes of the adsorption space W_0 and the coefficients of affinity β.

In spite of the already noted unfavorable shift of the upper limit of the range of applicability, the equation of the adsorption isotherm (1) satisfies the experimental data in a wide range of equilibrium relative pressures which in the majority of cases involve three orders of magnitudes. The limiting volumes of the adsorbent W_0 remain substantially constant on adsorption of the vapors of various substances. The mean values of limiting volumes are:

$$\text{for AG carbon } \overline{W_0} = 0.371 \pm 0.027 \text{ cm}^3/\text{g};$$

$$\text{for KAU carbon } \overline{W_0} = 0.497 \pm 0.037 \text{ cm}^3/\text{g}.$$

TABLE 2

Calculated and Experimental Values of Adsorption of Vapors in mM/g at Various Equilibrium Relative Pressures (AG carbon; $W_0 = 0.366$ cm^3/g; $B = 1.05 \cdot 10^{-6}$)

Vapor	Temperature in °C	β	$h = 1 \cdot 10^{-4}$		$h = 1 \cdot 10^{-3}$		$h = 1 \cdot 10^{-2}$	
			calc.	expt.	calc.	expt.	calc.	expt.
Benzene	20	1.00	0.97	0.96	1.83	1.75	2.87	2.86
Benzene	0	1.00	1.20	1.20	2.08	2.05	3.15	2.93
Cyclohexane	20	1.045	0.90	0.92	1.61	1.60	2.43	2.56
Cyclohexane	0	1.045	1.10	1.05	1.84	1.85	2.62	2.70
Toluene	20	1.33	1.53	1.52	2.18	2.10	2.81	2.78
Propane	20	0.715	0.24	0.21	0.85	0.97	2.06	2.30
n-Butane	20	0.865	0.54	0.58	1.26	1.30	2.30	2.34
n-Pentane	20	1.165	0.92	0.98	1.59	1.70	2.33	2.50
n-Pentane	0	1.165	1.10	1.27	1.76	1.94	2.47	2.63
n-Hexane	20	1.295	1.19	1.19	1.73	1.77	2.27	2.37
n-Heptane	20	1.460	1.19	1.32	1.60	1.77	1.97	2.28
Chloroform	20	0.865	0.66	0.73	1.54	1.53	2.81	2.80
Chloroform	0	0.865	0.81	0.85	1.68	1.78	2.83	3.12
Carbon tetrachloride	20	0.957	0.78	0.72	1.56	1.67	2.56	2.70
Ethyl chloride	20	0.71	—	—	1.03	1.03	2.52	2.43
Ethyl chloride	0	0.71	0.43	0.55	1.28	1.32	2.80	2.80
Methyl bromide	20	0.565	—	—	0.53	0.57	2.17	2.10

The maximum deviations from the mean values therefore do not exceed 8%.

The limiting volumes of the adsorption space ought to be compared with the volumes of the micropores of the carbons concerned:

$$\text{for AG carbon } v_{mi} = 0.384 \text{ cm}^3/\text{g};$$
$$\text{for KAU carbon } v_{mi} = 0.484 \text{ cm}^3/\text{g}.$$

The very close agreement between the limiting volumes of the adsorption space and the volumes of the micropores indicates that adsorption takes place in the adsorption space bounded by the walls of the micropores, and thereby affords a vivid illustration of the physical meaning of the concept of the limiting volumes of the adsorption space for active carbons of the first structural type.

TABLE 3

Calculated and Experimental Values of Adsorption of Vapors in mM/g at Various Equilibrium Relative Pressures (KAU carbon; $W_0 = 0.489$ cm^3/g; $B = 1.00 \cdot 10^{-6}$)

Vapor	Temperature in °C	β	$h = 1 \cdot 10^{-4}$		$h = 1 \cdot 10^{-3}$		$h = 1 \cdot 10^{-2}$	
			calc.	expt.	calc.	expt.	calc.	expt.
Benzene	20	1.00	1.39	1.35	2.54	2.51	3.90	3.93
Benzene	0	1.00	1.70	1.68	2.87	2.92	4.17	3.95
Cyclohexane	20	1.045	1.28	1.25	2.22	2.22	3.30	3.28
Cyclohexane	0	1.045	1.55	1.46	2.51	2.52	3.53	3.59
Toluene	20	1.33	2.09	2.16	2.96	2.92	3.79	3.66
Propane	20	0.715	0.38	0.33	1.23	1.30	2.84	3.17
n-Butane	20	0.865	0.79	0.73	1.77	1.78	3.14	3.35
n-Pentane	20	1.165	1.30	1.27	2.19	2.24	3.16	3.25
n-Pentane	0	1.165	1.55	1.62	2.43	2.53	3.35	3.45
n-Hexane	20	1.295	1.66	1.65	2.37	2.42	3.06	3.18
n-Heptane	20	1.46	1.74	1.88	2.31	2.45	2.83	2.98
Chloroform	20	0.865	0.96	0.98	2.15	2.20	3.81	3.94
Chloroform	0	0.865	1.26	1.17	2.33	2.65	4.20	4.30
Ethyl chloride	20	0.71	0.45	0.47	1.48	1.30	3.48	3.32
Ethyl chloride	0	0.71	0.65	0.67	1.83	1.72	3.85	3.70
Methyl bromide	20	0.565	—	—	0.80	0.78	3.05	2.85

The calculated coefficients of affinity (on the basis of the adsorption isotherms) of one and the same vapor on different carbons can likewise be considered identical in practice, since the maximum deviations from the mean values do not exceed 3% in the most unfavorable conditions.

Practical application of the equation of the adsorption isotherm (1) is bound up with determination of its constants W_0 and B from the experimental adsorption isotherm of the standard vapor (benzene) and with calculation of the adsorptions of other vapors under the given conditions (h, T). Definite interest is attached to evaluation of the possible deviations in such results when using the experimental values of the coefficients of affinity (the mean values in Table 1). With this objective, the isothermal equation (1) was used for calculation of the adsorptions of all of the investigated vapors at 20° and of some of them at 0° on AG and KAU carbons at three different equilibrium relative pressures. The only starting data were the constants W_0 and B calculated from the adsorption isotherms of benzene vapor; their values were (Table 1):

$$\text{AG carbon } W_0 = 0.366 \text{ cm}^3/\text{g}, \ B = 1.05 \cdot 10^{-6};$$
$$\text{KAU carbon } W_0 = 0.489 \text{ cm}^3/\text{g}, \ B = 1.00 \cdot 10^{-6}.$$

The physical constants of the adsorbates are given elsewhere [1, 3].

The calculated magnitudes of the adsorption were compared with those interpolated from the experimental isotherms, the graphs of which were obtained in a semi-logarithmic plot (a vs log p) on a sufficiently large scale. Calculated and experimental values are given in Tables 2 and 3 for adsorption on AG and KAU carbons (at 0° the adsorption isotherms of only a few of the vapors were measured).

The agreement between the calculated and measured values of adsorption can be considered satisfactory.

Relation of Adsorbability of Vapors to Their Physical Properties

Timofeev showed that to a first approximation the coefficient of affinity of the characteristic curves can be expressed by the ratio of the molar volume of the adsorbate in the liquid state v to the molar volume of the standard substance v_0 (benzene):

$$\beta = \frac{v}{v_0}. \tag{9}$$

If, however, the molar volumes of the substances are taken under conditions of identical internal pressures, then we can expect a better correspondence. This idea prompted Vaskovsky [8] to express the coefficient of affinity by the ratio of the parachors of the substances:

$$\beta = \frac{P}{P_0}, \tag{10}$$

where P_0 is the parachor of the standard substance (benzene).

From the data of Table 4 it follows that the so-calculated coefficients of affinity of the majority of the vapors are in satisfactory agreement with the experimental values. The greatest deviation is observed for vapors of cyclohexane and toluene (approximately 10%). Allowance must be made for the error when calculating the magnitude of adsorption under the most unfavorable conditions in view of these considerable deviations. Thus, for cyclohexane vapor and KAU carbon when $h = 1 \cdot 10^{-4}$, the experimental value of the adsorption is a = 1.25 mM/g; the calculated values are (for β = 1.045) a = 1.28 mM/g and(for β = 1.17) a = 1.64 mM/g.

TABLE 4

Approximate Estimate of the Affinity Coefficients of the Characteristic Curves

Vapor	β (expt.)	v/v_0	P/P_0
Benzene	1.00	1.00	1.00
Cyclohexane	1.05	1.21	1.17
Toluene	1.33	1.19	1.19
Propane	0.72	0.99	0.73
n-Butane	0.87	1.10	0.92
n-Pentane	1.08	1.29	1.11
n-Hexane	1.29	1.46	1.29
n-Heptane	1.46	1.65	1.48
Chloroform	0.87	0.90	0.89
Carbon tetrachloride	0.96	1.08	1.07
Ethyl chloride	0.71	0.80	0.72
Methyl bromide	0.57	0.62	0.60

Consequently, a deviation of 11% in the affinity coefficient leads to a 28% error when calculating the adsorption under the conditions stated. Similarly, for toluene vapor and AG carbon at $h = 1 \cdot 10^{-4}$ the experimental value was $a = 1.52$ mM/g and the calculated values were 1.53 mM/g (for $\beta = 1.33$) and 1.25 mM/g (for $\beta = 1.19$). In this case a 10% deviation in the affinity coefficient leads to an 18% error in the calculated value of adsorption. Errors of 20-25% are possible in many cases when the magnitude of adsorption is roughly evaluated. It should be noted that the differences between calculated and experimental values decrease at higher relative pressures.

Role of the Structure of the Active Carbon in the Adsorption Process

Both of the constants W_0 and B of the adsorption isotherm equation (1) depend upon the porous structure of the active carbon. It was already shown above that the limiting volumes of the adsorption space W_0 for active carbons of the first type of structure substantially coincide with the volumes of their micropores. The constant B reflects that quality of the porous system of the adsorbent that governs the effect of increase of the adsorption potentials. In the simplest model this quality is represented by the dimensions of the micropores. The smaller the constant B the more steeply does the curve of the isotherm rise in the initial pressure region.

Substituting in Eq. (1) the volume of the micropores of the carbon for the substantially equal adsorption space, we obtain the approximate equation:

$$a = a_0 F, \tag{11}$$

where

$$a_0 = \frac{V_{mi}}{v} \tag{12}$$

is the limiting magnitude of adsorption, corresponding to filling of the micropores with liquefied vapor, and

$$F = e^{-B\frac{T^2}{\beta^2}(\lg p_s/p)^2} \tag{13}$$

is the filling factor which represents the proportion of filling of the micropores under the given experimental conditions (h, T).

TABLE 5

Proportion of Space of Micropores Filled on Adsorption of Different Vapors at Various Relative Pressures at 20°

$B\cdot10^6$	β	F		
		$h = 1\cdot10^{-4}$	$h = 5\cdot10^{-3}$	$h = 1\cdot10^{-1}$
0.4	0.5	0.111	0.483	0.871
0.8		0.012	0.233	0.759
1.2		0.0014	0.113	0.662
0.4	1.0	0.577	0.834	0.966
0.8		0.333	0.695	0.933
1.2		0.193	0.582	0.912
0.4	1.5	0.783	0.923	0.985
0.8		0.614	0.851	0.971
1.2		0.481	0.785	0.955

It is interesting to consider the magnitudes of the filling factors when vapors of different types are adsorbed on active carbons whose structure changes within limits possible in practice, as governed by the values of the constants B ($0.4 \cdot 10^{-6}$ to $1.2 \cdot 10^{-6}$). Examples of vapors differing in adsorbability are heptane ($\beta = 1.46$), benzene ($\beta = 1.00$) and methyl bromide ($\beta = 0.57$).

Table 5 contains the values, calculated with Eq. (13), for the factors of filling of the space of the micropores of active carbons of different structures at 20° at different equilibrium relative pressures which change.

Table 5 indicates that in the case of highly adsorbable vapors at sufficiently high equilibrium relative pressures the filling factors of the micropores are close to unity independently of the values of constant B of the adsorption isotherm equation. In such cases the degree of adsorption of a vapor is mainly governed by the development of the volume of the micropores of the carbon, the dimensions of the latter being of secondary importance.

For less strongly adsorbable vapors at low equilibrium pressures, the factors of filling are small (some hundredths); their values are strongly dependent upon the constants B of the isothermal equation; this influence upon the degree of adsorption of vapors is definitely important. Development of the volume of the micropores plays a secondary part.

On the basis of these considerations it is possible to choose the active carbon most suitable for a particular industrial application.

Corresponding Conditions in Adsorption of Vapors

The experimentally proved applicability of the adsorption isotherm equation (1) over a wide range of equilibrium relative pressures enables us to derive a correlation between the magnitudes of adsorption or relative pressures during adsorption in the general case of different vapors on different specimens of active carbons under specific conditions. Starting from the linear form of the adsorption isotherm equation (4), we easily obtain;

for the condition of equality of the relative pressures:

$$\lg a_2 = \frac{C_2 D_1 - C_1 D_2}{D_1} - \frac{D_2}{D_1} \lg a_1 \tag{14}$$

for conditions of equality of adsorption

$$H_2^2 = \frac{C_2 - C_1}{D_2} + \frac{D_1}{D_2} H_1^2 . \tag{15}$$

When the filled volumes of the adsorption space are the same,

$$W_2 = W_1$$

or

$$\frac{a_2}{a_1} = \frac{v_1}{v_2} = \text{const} \tag{16}$$

We then have the following relation between equilibrium relative pressures:

$$H_2^2 = \frac{1}{D_2} \lg \frac{W_0''}{W_0'} + \frac{D_1}{D_2} H_1^2. \tag{17}$$

TABLE 6

Comparison of Adsorption Values for Various Vapors at Corresponding Equilibrium Relative Pressures

Carbon	1st vapor			2d vapor			a_1 in mM/g	a_2 in mM/g	$\frac{a_2}{a_1}$	$\frac{v_1}{v_2}$
	Formula	T_1	h_1	Formula	T_2	h_2				
AG	CH_3Br	293	$1 \cdot 10^{-1}$	C_6H_6	293	$1.85 \cdot 10^{-2}$	5.42	3.19	0.59	0.62
KAU	CH_3Br	293	$1 \cdot 10^{-1}$	C_6H_6	293	$1.85 \cdot 10^{-2}$	6.80	4.28	0.63	0.62
AG	CH_3Br	293	$1 \cdot 10^{-1}$	C_7H_{16}	293	$1.31 \cdot 10^{-3}$	5.42	1.82	0.34	0.37
KAU	CH_3Br	293	$1 \cdot 10^{-1}$	C_7H_{16}	293	$1.31 \cdot 10^{-3}$	6.80	2.50	0.37	0.37
AG	C_6H_{14}	293	$1 \cdot 10^{-4}$	C_2H_5Cl	273	$1.84 \cdot 10^{-3}$	1.18	1.60	1.35	1.85
KAU	C_6H_{14}	293	$1 \cdot 10^{-4}$	C_2H_5Cl	273	$1.84 \cdot 10^{-3}$	1.64	1.22	1.35	1.85
AG	$CHCl_3$	293	$1 \cdot 10^{-3}$	C_6H_{12}	273	$2.53 \cdot 10^{-4}$	1.53	1.32	0.86	0.76
KAU	$CHCl_3$	293	$1 \cdot 10^{-3}$	C_6H_{12}	273	$2.53 \cdot 10^{-4}$	2.20	1.86	0.85	0.76

For the special case of adsorption of different vapors on one and the same specimen of active carbon $W_0'' = W_0'$, Eq. (17) becomes much simpler and acquires the form:

$$H_2 = \frac{\beta_2 T_1}{\beta_1 T_2} H_1. \tag{18}$$

Since no terms associated with the properties of the active carbons enter into Eqs. (16) and (18), they are valid for any specimens of carbons. A constant ratio will therefore exist between the magnitudes of adsorption on any specimens of active carbons of two vapors if their relative pressures h_2 and h_1 are governed by the condition of Eq. (18) through Eq. (3). Such relative pressures may be called corresponding pressures.

Corresponding pressures of some vapors are enumerated in Table 6. Adsorptions of the vapors, interpolated from the experimental isothermal curve (plotted with semi-logarithmic coordinates), are in substantially constant ratios both for AG carbon and KAU carbon. The ratio of the adsorption values, however, does not always agree sufficiently closely with the reciprocal ratio of the molar volumes of the substances in the liquid state.

SUMMARY

1. Considerable experimental material is presented which shows the conformity with experimental results of the developed potential theory of adsorption of vapors. The ranges of applicability of the main equations is evaluated.

2. An examination is made of the relation between adsorbability of vapors and their physical properties, and consideration is given to a number cf effects that characterize the adsorptive behavior of vapors on active carbons.

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THE KINETICS OF OXIDATION OF FATS

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The study of the kinetics and mechanism of oxidation of fats is undoubtedly a task of great theoretical and practical importance. From the theoretical aspect the oxidation of fats is one of the special cases of oxidation of hydrocarbons. It is definitely known that in fat molecules the hydrocarbon radical linked to the triglyceride group preferentially undergoes oxidation. The oxidation starts, moreover, in that part of the radical which is separated from the triglyceride residue by a long chain of CH_2 groups, so that the oxygen-containing portion of the fat molecules, at least in the early stages of the process, cannot exert any influence on the course of oxidation. The oxidation of the hydrocarbon radicals entering into the composition of fat molecules proceeds in substantially the same manner as the oxidation of hydrocarbons of similar structure. Consequently, any new data on the kinetics and mechanism of oxidation of fats are a contribution to the study of the process of oxidation of hydrocarbons in general.

Apart from this aspect, the oxidation of fats in itself is invested with interest. It is an important biological process and is a problem in connection with food preservation. Oxidative processes, which take place in a fat even at temperatures below zero, ultimately lead to breakdown of the fat. Knowledge of the mechanism of oxidation of fats would enable us to eliminate the factors favorable to development of oxidative processes and, conversely, to suppress oxidation. In collaboration with Piulskaya, we recently, in the course of development of an accelerated method of testing of the resistance of fats to oxidative breakdown, obtained some results concerning the kinetics of oxidation of fats in the initial stage of the process [1]. We also investigated the inhibiting action of butylhydroxyanisole on fat oxidation [2].

The present paper is devoted to a presentation of the fundamental kinetic results that we obtained in the course of this investigation. It also contains fresh data on the development of the oxidation in more advanced stages.

EXPERIMENTAL

We selected lard as the material for oxidative studies since it is oxidized with facility and the problem of inhibition of its oxidative breakdown is a particularly important one. This fat is essentially a mixture of triglycerides of stearic (12-16%), palmitic (25-30%), oleic (41-51%), linoleic (3-8%), linolenic and arachidic (up to 2%) acids [3]. The high content of the three last highly unsaturated compounds is evidently responsible for facility of oxidation.

In order to exclude the action of various fortuitous factors which are unavoidable in the course of industrial melting, we started not from melted fat but from crude fat which was melted in the laboratory under vacuum and stored in vacuum until the moment of start of an experiment.

Oxidation was performed in an oxidation cell of molybdenum glass with a porous glass filter sealed to the base through which was forced a stream of air at a speed of 7-8 liters/hr. Into the cell was charged 25-50 g fat, and after definite periods of time samples were withdrawn from the cell and analyzed for their peroxide content by the usual iodometric method. This content was expressed by peroxide numbers as usually done for systems of complex chemical composition (a peroxide number of 1 is roughly equivalent to the formation of two hydroperoxide groups in 100 hydrocarbon radicals of a fat).

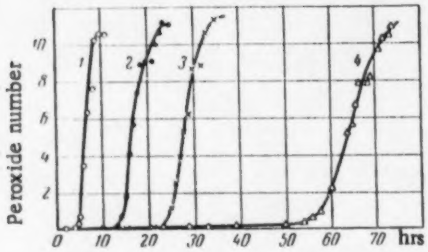

Fig. 1. Kinetic curves of accumulation of peroxides during oxidation of a fat at temperatures of: 1) 100°; 2) 90°; 3) 80°; 4) 70°.

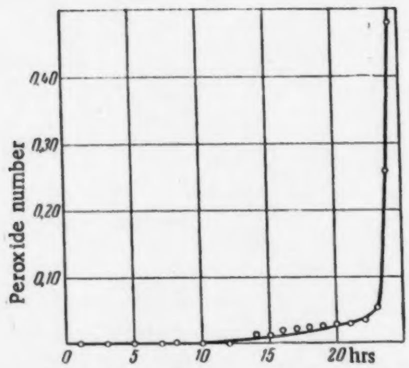

Fig. 2. Kinetic curve of accumulation of peroxides during oxidation of a fat at 90°.

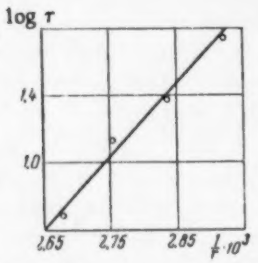

Fig. 3. Oxidation velocity as a function of temperature in the first stage of oxidation of a fat (τ is the interval of time for attainment of a peroxide number of 0.5).

As an antioxidant we chose tert.-butylhydroxyanisole (mixture of 3,4- and 2,4-isomers) which was synthesized by the method described in our preceding paper [2]. We chose this antioxidant because it is extensively used abroad for stabilization of edible products and is therefore a product of industrial importance.

The kinetic curves representing the accumulation of peroxides on oxidation of the fat at various temperatures are plotted in Fig. 1. The data show that the process goes in two stages: in the first stage oxidation is relatively slow with weak self-acceleration, while in the second stage the reaction is rapid, and the attainment of peroxide values of the order of 0.1-0.5 is accompanied by the vigorous onset of oxidation which leads in a short time to increase in the peroxide number by a factor of several tens. When the peroxide number reaches a value of 10, the rate of formation of peroxides slows down and (Fig. 8) the concentration of peroxides passes through a maximum. The kinetic curve of oxidation of one of the fat specimens is plotted on an enlarged scale in Fig. 2 at different stages of oxidation. This scale clearly reveals the transition from slow to rapid oxidation. This transition becomes less abrupt when the temperature is lowered, and at 70° there is substantially no sharp discontinutity on the kinetic curve.

An important kinetic characteristic of a reaction is known to be its activation energy. If different stages of the process were indeed involved, then we should expect the activation energy during the initial reaction period to differ from the energy during the period of rapid oxidation. Since the determination of the reaction velocity in its first period (when the peroxide numbers are still only several hundredths) is a very inaccurate operation, we select as measure of the velocity during this period the length of time τ from the start of oxidation to the attainment of a peroxide number of 0.5. The choice of the instant of completion of the first stage is to some extent arbitrary, but we can readily convince ourselves that this does not seriously affect the sought-for magnitude of activation energy. The value of τ is the reciprocal of the velocity of the process, and we can therefore expect $\log \tau$ to be a linear function of T^{-1}. We see from Fig. 3 that a linear dependence is actually found and the activation energy is 20.0 kcal.

The kinetic curves of the second oxidation stage are plotted in Fig. 4. The interval of time for attainment of a peroxide number of 0.5 is selected as the start for all of the curves. The maximum velocity of the second stage as a function of temperature is plotted in Fig. 5 with Arrhenius coordinates. The Arrhenius law is valid but the activation energy is considerably lower (14.5 kcal). This constitutes further evidence that we are dealing with two different stages during oxidation of a fat.

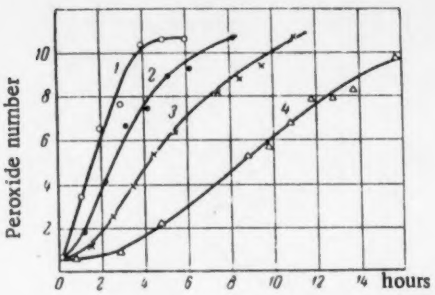

Fig. 4. Kinetics of accumulation of peroxides during the second stage of fat oxidation at temperatures of: 1) 100°; 2) 90°; 3) 80°; 4)70°.

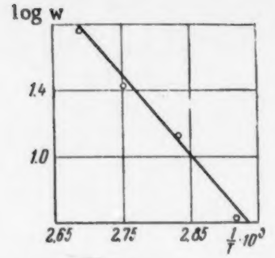

Fig. 5. Maximum velocity w of fat oxidation as a function of temperature during the second stage.

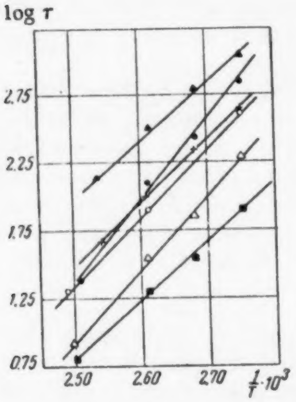

Fig. 6. Length of time τ for attainment of a peroxide number of 0.1 as a function of the temperature for different specimens of fat.

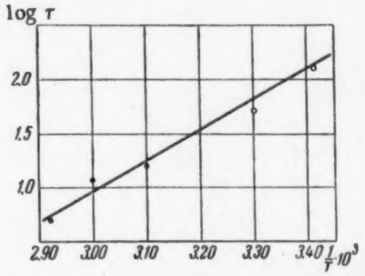

Fig. 7. Time τ of attainment of a peroxide number of 0.1 as a function of the temperature of oxidation of tallow in presence of 0.02% of cobalt stearate for fused (●) and solid (○) fat.

Since we are dealing with a complex system of biological origin, it was of interest to establish the variation in the fundamental kinetic characteristic (the activation energy of oxidation) from one specimen to another. This was established only for the first stage of fat oxidation, and in all cases the measure of velocity was the interval before attainment of a peroxide number of 0.1. In Fig. 6 (in Arrhenius coordinates) is plotted the length of time τ as a function of temperature. The slopes of the straight-line plots for the different specimens only vary slightly (in the range of 20-25 kcal).

Since fats are normally stored at low temperatures with the fat in the solid state, it was important to ascertain whether the relations established for oxidation of melted fats were also applicable to solid fats. With this objective we studied the kinetics of a single specimen of fat in the fused and solid states. The transition of lard from the liquid to the solid state takes place over a wide range of temperatures. Tallow was therefore used in this investigation. In view of the resistance of tallow to oxidation, 0.02 % of cobalt stearate (an oxidation catalyst) was added to it. Oxidation of the solid fat was effected in the same oxidation cell, but the fat was applied as a film on glass tubes which were put into the cell.

Figure 7 (Arrhenius coordinates) contains plots of the time τ for attainment of a peroxide number of 0.1 as a function of temperature. Points corresponding to the solid and liquid fat are seen to lie on one straight line, i. e., the change of physical state does not influence the fundamental kinetic constant of the fat (the activation energy). This behavior is evidence that the mechanism of the oxidation of the liquid fat is the same as that of the solid fat.

Kinetic curves of oxidation of lard at 100° without antioxidant and in presence of 0.01% of butylhydroxyanisole are plotted in Fig. 8. Addition of antioxidant is seen to considerably lengthen the first stage of the process.

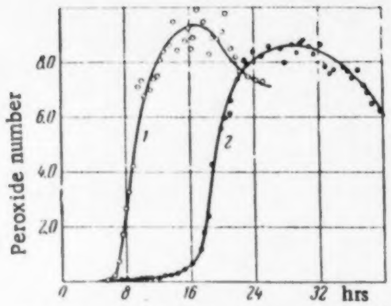

Fig. 8. Kinetics of oxidation of fat at 100° in the absence of antioxidant (curve 1) and in presence of 0.01% of butylhydroxyanisole (curve 2).

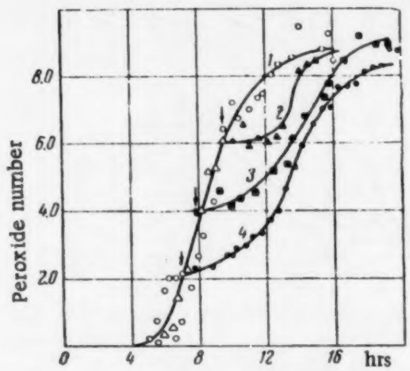

Fig. 9. Kinetics of accumulation of antioxidants during the second stage of oxidation of a fat in the absence of butylhydroxyanisole (curve 1) and with addition of 0.01% of butylhydroxyansiole (curves 2-4). (The arrows indicate the instants of addition of antioxidant.)

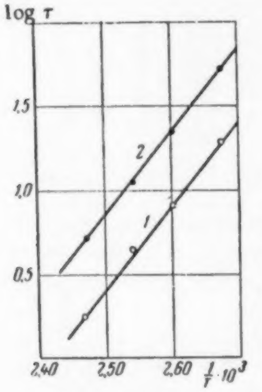

Fig. 10. Period τ for attainment of peroxide number of 0.1 as a function of the temperature for noninhibited fat (curve 1) and fat containing 0.02% of butylhydroxyanisole (curve 2).

After the oxidation had gone to a sufficient degree, the rapid stage of oxidation was initiated, and in the latter the reaction velocity was the same as in the absence of antioxidant. This is mainly due to the consumption of antioxidant during the first stage, i. e., the butylhydroxyanisole added during the second stage of the process appreciably inhibits the process (Fig. 9) but not for very long.

In Fig. 10 (Arrhenius coordinates) is plotted the period τ for attainment of a peroxide number of 0.1 as a function of the temperature for the noninhibited oxidation and for oxidation in presence of 0.02% of butylhydroxyanisole. The curves run parallel, indicating that the activation energies of inhibited and noninhibited oxidation are identical. In the present case the energy is 23 kcal/mole.

Evaluation of the Experimental Results

The abrupt rise in velocity of oxidation of a fat when peroxide numbers of the order of 0.1-0.5 had been reached, as well as the change in the activation energy of the process indicate that we are dealing with two stages of the process of formation of peroxides, each stage having a different mechanism. The investigated fat contains a large quantity of unsaturated compounds which in the pure form are oxidized with great facility (for example, ethyl linoleate is oxidized with appreciable velocity even at 35° [4]). The relatively slow oxidation of a fat at temperatures up to 100° and higher (with a long induction period) points to the presence in the fat of traces of certain inhibitors. This surmise is supported by the identity in the activation energies of uninhibited and inhibited oxidation of the fat. The rate of formation of peroxides is actually governed by the velocity of the reaction

$$RO^{\cdot}_2 + RH \rightarrow ROH_2 + R^{\cdot},$$

where RH is the original fat.

$$W = k_1 [RH] [RO_2].$$

If the system does not contain inhibitors, the chains are broken through recombination of RO_2 radicals, and then:

$$w_{init} = k_2 [RO_2]^2,$$

where w_{init} is the velocity of initiation; k_2 is the velocity constant of recombination.

In presence of inhibitor, chain-breaking takes place due to collision of RO_2 radicals with molecules of inhibitor I, and then:

$$w_{init} = k_i [RO_2][I].$$

Consequently, in the absence of inhibitor:

$$w = w_{init}^{1/2} \frac{k_1}{k_2^{1/2}} [RH],$$

and in presence of inhibitor:

$$w = w_{init} \frac{k_1}{k_i[I]} [RH].$$

The activation energies of the respective processes may then be written thus:
without inhibitor:

$$E = \frac{1}{2} E_{init} + E_1;$$

with inhibitor:

$$E = E_{init} + E_1 - E_i.$$

Thus the expressions for the activation energy of the uninhibited and inhibited oxidation differ appreciably from one another. At the same time the introduction of butylhydroxyanisole into the system does not change the activation energy of the first stage of the process. This can be best explained on the assumption that the mechanism of the first stage is not appreciably altered by introduction of antioxidant, i. e., that the original fat contains some antioxidant of the same order of activity (i. e., with the same E_i) as butylhydroxyanisole. Since the initiation of oxidation is most probably realized through the breakdown of the peroxides, then E_{init} is the activation energy of breakdown of the peroxides, which in the case of ethyl linoleate hydroperoxide is equal to 26 kcal [4] (and linoleic acid is the main highly unsaturated component of the investigated fat); E_1 for linoleic acid is equal to 4 kcal, so that the value of E is 17 kcal. This value does not differ considerably from that found for the second stage of oxidation of the fat, and this makes it probable that the second stage is the uninhibited oxidation of the fat catalyzed by the breakdown of hydroperoxides.

On this basis, we obtain for the first stage:

$$E = 30 - E_i.$$

Since the observed activation energy of the first stage is of the order of 20-25 kcal, then for E_i we obtain a value of 5-10 kcal. This is a very probable value for a radical reaction with a molecule of an inhibitor.

Our data consequently indicate that the first macroscopic stage of fat oxidation is oxidation in presence of natural inhibitors present in the fat, while the second stage is associated with rapid development of the oxidative processes after decomposition of these inhibitors.

SUMMARY

1. Accumulation of peroxides during oxidation of a fat takes place in two stages. The first stage is a relatively slow reaction with weak auto-acceleration and an activation energy of 20-25 kcal. The second stage goes with high velocity until the concentration of peroxide reaches a maximum, and its activation energy is 14.5 kcal.

2. Addition of tert -butylhydroxyanisole considerably lengthens the first stage of oxidation without influencing its activation energy.

3. Introduction of butylhydroxyanisole at the second stage sharply inhibits the oxidation. After a short period, however, the reaction is renewed at high velocity evidently due to destruction of the inhibitor.

4. The occurrence of two stages of oxidation is evidently associated with the presence of a natural antioxidant in the fat, the destruction of this antioxidant leading to commencement of rapid oxidation.

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THE SYNTHESIS OF LIQUID (1−n)-HEXAMETHYLPOLYCHLOROPHENYLETHYL SILOXANES

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Organosilicon liquid polymers (polyorganosiloxanes) find extensive application in various branches of industry; they are used for the preparation of heat-resistant lubricating oils with low freezing points, hydraulic fluids, damping liquids, etc. The first liquid polyorganosiloxanes were made from alkyl-substituted esters of orthosilicic acid and alkylchlorosilanes [1-4]. A large group of liquid polymers was obtained from dimethyldichlorosilane and trimethylchlorosilane [5]. All of the liquid polyorganosiloxanes exhibit weak polar properties and their dielectric permittivity is in the range of 2.2 to 2.7. Definite theoretical and industrial interest is attached to studies aimed at the synthesis of liquid, heat-resistant, nonflammable polyorganosiloxanes with high dielectric permittivity. The development of a method of synthesis of such polymers necessitates increasing the asymmetry of the polymeric molecules, and this can be done (while retaining the main siloxane chain of the molecule) by introducing hetero atoms into the organic radicals. In this connection attention is merited by the introduction of chlorine into the phenyl radical at the silicon atom where the mobility of the chlorine is low so that the thermal and hydrolytic stability of the polymeric molecule is ensured.

Chlorophenylethyldichlorosilanes and trimethylchlorosilane were chosen as starting substances for the synthesis of liquid polymers. The former substance was prepared from phenyltrichlorosilane by chlorination with gaseous chlorine:

$$C_6H_5SiCl_3 + m\,Cl_2 \rightarrow Cl_mC_6H_{5-m}SiCl_3 + m\,HCl.$$

This reaction was used for the preparation of 3-chlorophenylethyldichlorosilane and 1,3,5-trichlorophenyltrichlorosilane. The ethyl group was added to chlorophenyltrichlorosilanes by the reaction [6]:

$$Cl_mC_6H_{5-m}SiCl_3 + C_2H_5MgBr \rightarrow Cl_mC_6H_{5-m}\underset{\substack{|\\ C_2H_5}}{SiCl_2} + MgClBr.$$

We prepared 3-chlorophenylethyldichlorosilane, 1,3-dichlorophenylethyldichlorosilane and 1,3,5-trichlorophenylethyldichlorosilane by this reaction.

Liquid polymers were synthesized by cohydrolysis of chlorophenylethyldichlorosilanes with trimethylchlorosilane according to the scheme:

$$n\,\begin{matrix}Cl_mC_6H_{5-m}\diagdown\\ C_2H_5\diagup\end{matrix}SiCl_2 + 2(CH_3)_3SiCl \xrightarrow{H_2O} (CH_3)_3SiO\,[\overset{\substack{Cl_mC_6H_{5-m}\\ }}{\underset{\substack{|\\ C_2H_5}}{Si}} - O]_nSi\,(CH_3)_3 + 2(n+1)\,HCl,$$

where m = 1, 2, 3; n = 1, 2, 3, 4.

By varying the ratio of chlorophenylethyldichlorosilane to trimethylchlorosilane, we obtained polymers with degrees of polymerization corresponding to n = 1, 2, 3, 4. Trimethylchlorosilane was taken in excess in order to exclude cyclization of the productions of hydrolysis. New linear polymers were obtained whose composition and properties are detailed in the table.

TABLE

Name of substance	Formula	$K = \frac{\eta_{20}}{\eta_{120}}$	ε	Activation energy of viscous flow E_V(cal/mole)	n_D^{20}	d_4^{20}	MR	
							found	calculated
1,3-Hexamethyl-2-phenyl-2-ethyltrisiloxane	$(CH_3)_3\,SiO\,\underset{C_2H_5}{\overset{C_6H_5}{[SiO]}}\,Si\,(CH_3)$	3.18	2.61	2666	1.4830	1.0234	87.2	92.37
1,3-Hexamethyl-2-chlorophenyl-2-ethyltrisiloxane	$(CH_3)_3\,SiO\,\underset{C_2H_5}{\overset{ClC_6H_4}{[SiO]_1}}\,Si\,(CH_3)_3$	7.0	3.46	4377	1.4854	1.0541	97.23	94.26
1,4-Hexamethyl-2,3-dichlorophenyl-2,3-diethyltetrasiloxane	$(CH_3)_3\,SiO\,\underset{C_2H_5}{\overset{ClC_6H_4}{[SiO]_2}}\,Si\,(CH_3)_3$	9.73	3.61	5207	1.5002	1.0634	143.7	147.0
1,5-Hexamethyl-2,3,4-trichlorophenyl-2,3,4-triethylpentasiloxane	$(CH_3)_3\,SiO\,\underset{C_2H_5}{\overset{ClC_6H_4}{[SiO]_3}}\,Si\,(CH_3)_3$	11.6	3.80	5610	1.5030	1.1206	190.3	190.8
1,6-Hexamethyl-2,3,4,5-tetrachlorophenyl-2,3,4,5-tetraethylhexasiloxane	$(CH_3)_3\,SiO\,\underset{C_2H_5}{\overset{ClC_6H_4}{[SiO]_4}}\,Si\,(CH_3)_3$	28.89	3.96	7702	1.5098	1.1537	236.8	233.2
1,3-Hexamethyl-2-dichlorophenyl-2-ethyltrisiloxane	$(CH_3)_3\,SiO\,\underset{C_2H_5}{\overset{Cl_2C_6H_3}{[SiO]}}\,Si\,(CH_3)_3$	10.46	3.41	5373	1.4963	1.1176	192.4	99.6

1,4-Hexamethyl-2,3-di-(dichlorophenyl)-2,3-diethyltetrasiloxane	$(CH_3)_3SiO[\overset{C_6H_3Cl_2}{\underset{C_2H_5}{Si}}O]_2Si(CH_3)_3$	25.68	3.56	7427	1.5118	1.1636	153.5	154.6
1,5-Hexamethyl-2,3,4-tri-(dichlorophenyl)-2,3,4-triethylpentasiloxane	$(CH_3)_3SiO[\overset{Cl_2C_6H_3}{\underset{C_2H_5}{Si}}O]_3Si(CH_3)_3$	62.27	3.64	9452	1.5250	1.1831	204.8	212.0
1,6-Hexamethyl-2,3,4,5-tetra-(dichlorophenyl)-2,3,4,5-tetraethylhexasiloxane	$(CH_3)_3SiO[\overset{Cl_2C_6H_3}{\underset{C_2H_5}{Si}}O]_4Si(CH_3)_3$	97.49	3.73	10480	1.5350	1.2620	256.2	255.9
1,3-Hexamethyl-2-trichlorophenyl-2-ethyltrisiloxane	$(CH_3)_3SiO[\overset{Cl_3C_6H_2}{\underset{C_2H_5}{Si}}O]Si(CH_3)_3$	18.53	3.77	6680	1.5150	1.2012	106.9	105.2
1,4-Hexamethyl-2,3-di-(trichlorophenyl)-2,3-diethyltetrasiloxane	$(CH_3)_3SiO[\overset{Cl_3C_6H_2}{\underset{C_2H_5}{Si}}O]_2Si(CH_3)_3$	50.45	3.86	8969	1.5280	1.2507	164.98	164.46
1,5-Hexamethyl-2,3,4-tri-(trichlorophenyl)-2,3,4-triethylpentasiloxane	$(CH_3)_3SiO[\overset{Cl_3C_6H_2}{\underset{C_2H_5}{Si}}O]_3Si(CH_3)_3$	326.69	3.96	13240	1.5316	1.3397	223.0	216.8
1,6-Hexamethyl-2,3,4,5-tetra-(trichlorophenyl)-2,3,4,5-tetraethylhexasiloxane	$(CH_3)_3SiO[\overset{Cl_3C_6H_2}{\underset{C_2H_5}{Si}}O]_4Si(CH_3)_3$	—	3.98	—	1.5470	1.3435	281.0	277.5

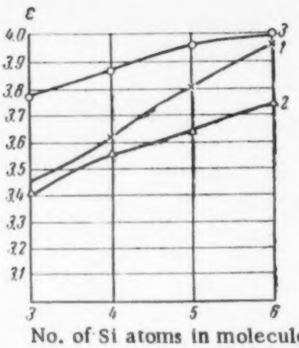

Fig. 1. Relation between dielectric permittivity and number of silicon atoms in molecule:

$1 - (CH_3)_3SiO[\underset{C_2H_5}{\overset{ClC_6H_4}{SiO}}]_n Si(CH_3)_3;$

$2 - (CH_3)_3SiO[\underset{C_2H_5}{\overset{Cl_2C_6H_3}{SiO}}]_n Si(CH_3)_3;$

$3 - (CH_3)_3SiO[\underset{C_2H_5}{\overset{Cl_3C_6H_2}{SiO}}]_n Si(CH_3)_3$

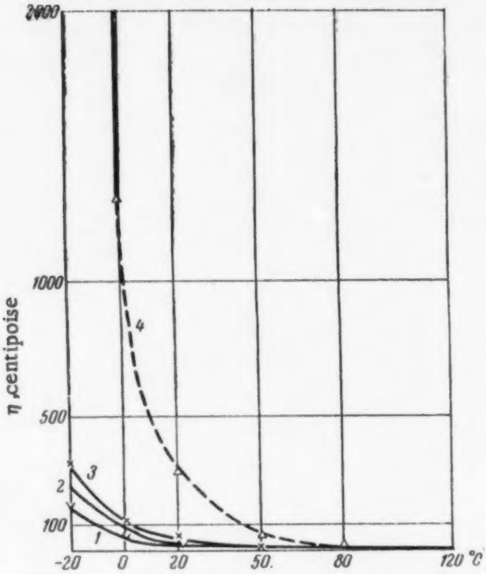

Fig. 2. Viscosity as a function of temperature: 1) 1,3-hexamethyl-2-chlorophenyl-2-ethyltrisiloxane; 2) 1,4-hexamethyl-2,3-dichlorophenyl-2,3-diethyltetrasiloxane; 3) 1,5-hexamethyl-2,3,4-trichlorophenyl-2,3,4-triethylpentasiloxane; 4) 1,6-hexamethyl-2,3,4,5-tetrachlorophenyl-2,3,4,5-tetraethylhexasiloxane.

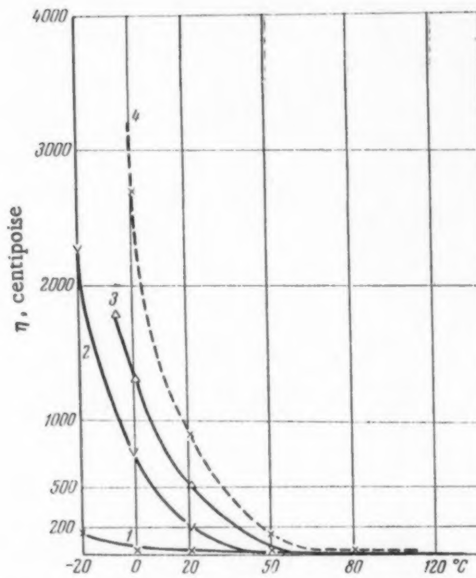

Fig. 3. Viscosity as a function of temperature: 1) 1,3-hexamethyl-2-dichlorophenyl-2-ethyltrisiloxane; 2) 1,4-hexamethyl-2,3-di-(dichlorophenyl)-2,3-diethyltetrasiloxane; 3) 1,5-hexamethyl-2,3-4-tri-(dichlorophenyl)-2,3,4-triethylpentasiloxane; 4) 1,6-hexamethyl-2,3,4,5-tetra-(dichlorophenyl)-2,3,4,5-tetraethylhexasiloxane.

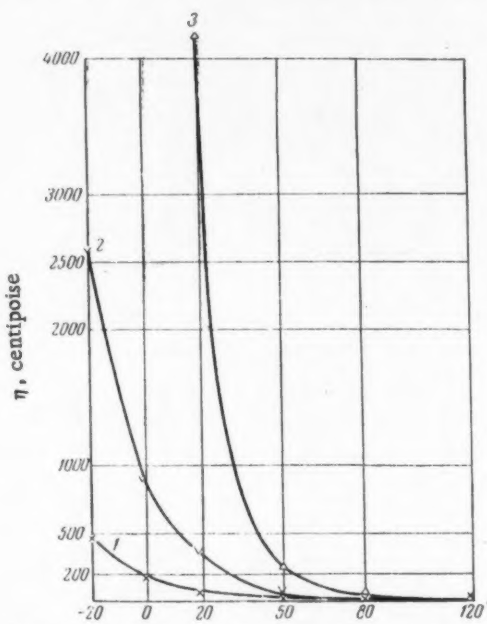

Fig. 4. Viscosity as a function of temperature: 1) 1,3-hexamethyl-2-trichlorophenyl-2-ethyltrisiloxane; 2) 1,4-hexamethyl-2,3-di-(trichlorophenyl)-2,3-diethyltetrasiloxane; 3) 1,5-hexamethyl-2,3,4-tri-(trichlorophenyl)-2,3,4-triethylpentasiloxane.

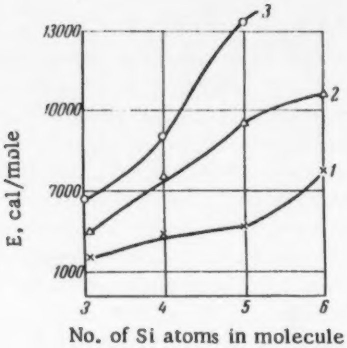

Fig. 5. Energy of activation of viscous flow as a function of the number of silicon atoms in the molecule:

$1 - (CH_3)_3SiO[Si(ClC_6H_4)(C_2H_5)O]_n Si(CH_3)_3$;

$2 - (CH_3)_3SiO[Si(Cl_2C_6H_3)(C_2H_5)O]_n Si(CH_3)_3$;

$3 - (CH_3)_3SiO[Si(Cl_3C_6H_2)(C_2H_5)O]_n Si(CH_3)_3$

The table shows that the introduction of chlorine atoms into the phenyl radical changes the electrical symmetry of the molecules and leads to a considerable rise in dielectric permittivity; thus, the dielectric constant of 1,3-hexamethyl-2-phenyl-2-ethyltrisiloxane is 2.6; that of 1,3-hexamethyl-2-chlorophenyl-2-ethyltrisiloxane is 3.46; that of 1,3-hexamethyl-2-dichlorophenyl-2-ethyltrisiloxane is 3.41; that of 1,3-hexamethyl-2-trichlorophenyl-2-ethyltrisiloxane is 3.77. Increasing number of links in the polymeric molecule is accompanied by higher dielectric permittivity (see Fig. 1). The temperature coefficient of viscosity of hexamethylchlorophenylsiloxanes alters sharply not only with increasing length of polymer chain but also with increasing number of chlorine atoms at the phenyl radical when the number of atoms of silicon in the molecule is unchanged.

In the case of 1,3-hexamethyl-2-phenyl-2-ethyltrisiloxane for example, the temperature coefficient of viscosity (for the range of 20-120°) is 3.18, in the case of 1,3-hexamethyl-2-chlorophenyl-2-ethyltrisiloxane it is 7.0, in the case of 1,3-hexamethyl-2-dichlorophenyl-2-ethyltrisiloxane it is 10.46, and in the case of 1,3-hexamethyl-2-trichlorophenyl-2-ethyltrisiloxane it is 18.53. This sharp rise in the temperature coefficient of viscosity is due to the increase of the energies of intramolecular interaction in the compounds. Viscosities are plotted as functions of the temperature of (1−n)-hexamethylchlorophenylethylsiloxanes in Figs. 2-4.

Calculations of the activation energy of viscous flow E_{visc}, carried out with the help of the Arrhenius equation $\eta = Ae^{\frac{E}{kT}}$, , showed that in the (1−n)-hexamethylchlorophenylethylsiloxanes that we investigated this energy increases with growth of the polymer chain (Fig.5). This energy also increases with increasing number of chlorine atoms in the phenyl radical; the following values of E_{visc} are found for polymers of the same chain length: 2.66 kcal/mole for 1,3-hexamethyl-2-phenyl-2-ethyltrisiloxane; 4.37 kcal/mole for 1,3-hexamethyl-2-chlorophenyl-2-ethyltrisiloxane; 5.37 kcal/mole 1,3-hexamethyl-2-dichlorophenyl-2-ethyltrisiloxane; 6.68 kcal/mole for 1,3-hexamethyl-2-trichlorophenyl-2-ethyltrisiloxane. According to literature data, the E_{visc} of 1,4-hexamethyl-2,3-tetramethyltetrasiloxane is 2.51 kcal/mole [7, 8].

EXPERIMENTAL

The following compounds were used in the investigation: trimethylchlorosilane, b. p. 56-58°, 35.5% Cl'; 3-chlorophenylethyldichlorosilane, b. p. 116-118° (7 mm), 30% Cl'; 1,3-dichlorophenylethyldichlorosilane, b. p. 130-132° (10 mm), 26.2% Cl'; 1,3,5-trichlorophenylethyldichlorosilane, b. p. 142-144° (12 mm), 24% Cl'; toluene, b. p. 109-111°.

1,3-Hexamethyl-2-chlorophenyl-2-ethyltrichlorosilane. In a three-necked flask, fitted with dropping funnel, thermometer, reflux condenser and stirrer, were placed 400 g water and 100 g toluene. The contents of the flask were heated to 90-95° and a mixture of 100 g (0.41 mole) chlorophenylethyldichlorosilane, 108.5 g (1 mole) trimethylchlorosilane and 100 g toluene was added dropwise with intensive stirring. Reaction was effected by boiling the mixture for 2-3 hours. After completion of the reaction, the product was cooled, transferred to a separating funnel and washed free of hydrochloric acid (until the reaction for the chloride ion was negative). The toluene solution was then separated from the aqueous layer and transferred to a Claisen flask from which the toluene was driven off. The residual organosilicon liquid was distilled in vacuum. Analysis was performed on the fraction with b. p. 120-130° (3 mm); n_D^{20} 1.4854; d_4^{20} 1.0541.

Found %: C 48.9, 48.6; H 7.25, 7.88; Si 21.25, 21.29; Cl 9.85, 10.15. $C_{14}H_{27}O_2Si_3Cl$. Calculated %: C 48.5; H 7.8; Si 24.2; Cl 10.2.

1,4-Hexamethyl-2,3-dichlorophenyl-2,3-diethyltetrasiloxane. 300 g water and 75 g toluene were placed in a reaction flask, the contents were heated to the boil, and dropwise addition was made with intensive stirring of a mixture of 100 g (0.41 mole) chlorophenylethyldichlorosilane, 55 g (0.509 mole) trimethylchlorosilane and 75 g toluene. Reaction period 2-2.5 hours. During the reaction the temperature was held at 90-95°. After completion of the reaction, the mixture was transferred to a separating funnel and washed free of hydrochloric acid. The toluene was then driven off by heating to 140-150°. The residual organosilicon liquid was colored; it could not be fractionated in vacuum at 2-3 mm; the residual polymer was therefore purified with "kil" activated clay, using 5-8 wt.% of the latter (the actual proportion being governed by the color of the liquid – 5% if light-colored, 8% for liquids with darker colors). This purification operation was carried out in a small round-bottomed flask fitted with thermometer and stirrer. The mixture of organosilicon liquid and "kil" was vigorously stirred for 30-40 min at 160-170° with simultaneous distillation of the low-boiling components. The reaction mixture was then cooled and filtered in vacuum; the purified, colorless or light-yellow liquid was analyzed for its content of carbon, hydrogen, silicon and chlorine; its specific gravity and refractive index were determined; the temperature dependence of the viscosity and some electrical characteristics were measured.

Hydrolysis gave 90 g of 1,4-hexamethyl-2,3-dichlorophenylethyl-2,3-diethyl-tetrasiloxane or 81% of theory; n_D^{20} 1.5002, d_4^{20} 1.0634.

Found %: C 47.44, 47.96; H 6.64, 6.54; Si 22.* , 21.70; Cl 12.9, 12.8. $C_{22}H_{36}O_3Si_4Cl_2$. Calculated %: C 49.7; H 7.1; Si * . ; Cl 13.6.

1,5-Hexamethyl-2,3,4-trichlorophenyl-2,3,4-triethylpentasiloxane. This was prepared and purified by the method detailed above, starting from 100 g (0.41 moles) chlorophenylethyldichlorosilane and 36 g (0.33 mole) trimethylchlorosilane; yield 70%; n_D^{20} 1.5030; d_4^{20} 1.1206.

Found %: C 50.2, 50.24; H 5.92, 6.30; Si 19.34, 19.02; Cl 13.04, 13.29. $C_{30}H_{45}O_4Si_5Cl_3$. Calculated %: C 50.46; H 6.29; Si 19.57; Cl 14.86.

1,6-Hexamethyl-2,3,4,5-tetrachlorophenyl-2,3,4,5-tetraethylhexasiloxane. This was prepared and purified as described above, starting from 100 g (0.41 mole) chlorophenylethyldichlorosilane and 30 g (0.27 mole) trimethylchlorosilane. Yield 70%; n_D^{20} 1.5098; d_4^{20} 1.1537.

Found %: C 49.14, 49.24; H 5.80, 5.86; Si 18.99, 18.70; Cl 15.7, 15.6. $C_{38}H_{54}O_5Si_6Cl_4$. Calculated %: C 50.67; H 6.00; Si 18.68; Cl 15.75.

1,3-Hexamethyl-2-dichlorophenyl-2-ethyltrisiloxane. This was similarly prepared from 90 g (0.33 mole) dichlorophenylethyldichlorosilane and 86 g (0.79 mole) trimethylchlorosilane; yield 69%; n_D^{20} 1.4963; d_4^{20} 1.1176.

Found %: C 44.98, 45.04; H 6.73, 6.63; Si 21.48, 21.46; Cl 19.1, 19.5. $C_{14}H_{26}O_2Si_3Cl_2$. Calculated %: C 44.1; H 6.8; Si 22.05; Cl 18.7.

1,4-Hexamethyl-2,3-di-(dichlorophenyl)-2,3-diethyltetrasiloxane. Similarly synthesized from 120 g (0.44 mole) dichlorophenylethyldichlorosilane and 57 g (0.52 mole) trimethylchlorosilane; yield 80%; n_D^{20} 1.5118; d_4^{20} 1.1636.

Found %: C 45.1, 45.0; H 6.06, 5.98; Si 19.4, 19.4; Cl 23.1, 23.3. $C_{22}H_{34}O_3Si_4Cl_4$. Calculated %: C 44.0; H 6.0; Si 18.7; Cl 23.6.

1,5-Hexamethyl-2,3,4-tri-(dichlorophenyl)-2,3,4-triethylpentasiloxane. Similarly prepared from 200 g (0.72 mole) dichlorophenylethyldichlorosilane and 63.5 g (0.59 mole) trimethylchlorosilane; yield 83%; n_D^{20} 1.5250; d_4^{20} 1.1831.

* [The omitted numbers were illegible in the original – Publisher.]

Found %: C 44.3, 44.5; H 5.27, 5.23; Si 16.95, 17.03; Cl 25.9, 25.7. $C_{30}H_{42}O_4Si_5Cl_6$. Calculated %: C 43.97; H 5.13; Si 17.1; Cl 25.98.

1,6-Hexamethyl-2,3,4,5-tetradichlorophenyl-2,3,4,5-tetraethylhexasiloxane. Similarly prepared from 120 g (0.44 mole) dichlorophenylethyldichlorosilane and 31 g (0.28 mole) trimethylchlorosilane; yield 75%; n_D^{20} 1.5350; d_4^{20} 1.2620.

Found %: C 43.84, 44.14; H 4.62, 4.36; Si 15.4, 15.7; Cl 26.87, 26.62. $C_{38}H_{50}O_5Si_6Cl_8$. Calculated %: C 43.94; H 4.81; Si 16.19; Cl 27.33.

1,3-Hexamethyl-2-trichlorophenyl-2-ethyltrisiloxane. Prepared as above from 50 g (0.16 mole) trichlorophenylethyldichlorosilane and 42.2 g (0.39 mole) trimethylchlorosilane; yield 82%; n_D^{20} 1.5150; d_4^{20} 1.2012.

Found %: C 40.51, 40.71; H 5.66, 5.74; Si 19.6, 19.6; Cl 25.9, 26.2. $C_{14}H_{25}O_2Si_3Cl_3$. Calculated %: C 40.44; H 6.0; Si 20.2; Cl 25.6.

1,4-Hexamethyl-2,3-di-(trichlorophenyl)-2,3-diethyltetrasiloxane. Similarly synthesized from 50 g (0.16 mole) trichlorophenylethyldichlorosilane and 21 g (0.19 mole) trimethylchlorosilane; yield 73%; n_D^{20} 1.5280; d_4^{20} 1.2507.

Found %: C 40.54, 40.65; H 3.98, 4.07; Si 16.12, 16.38; Cl 31.42, 31.56. $C_{22}H_{32}O_3Si_4Cl_6$. Calculated %: C 40.5; H 4.53; Si 16.7; Cl 31.8.

1,5-Hexamethyl-2,3,4-tri-(trichlorophenyl)-2,3,4-triethylpentasiloxane. Prepared as above from 70 g (0.22 mole) trichlorophenylethyldichlorosilane and 20 g (0.18 mole) trimethylchlorosilane; yield 70%; n_D^{20} 1.5316; d_4^{20} 1.3397.

Found %: C 40.58, 40.42; H 4.42, 4.13; Si 14.73, 14.93; Cl 34.64, 35.43. $C_{30}H_{39}O_4Si_5Cl_9$. Calculated%: C 39.0; H 4.23; Si 15.1; Cl 34.6.

1,6-Hexamethyl-2,3,4,5-tetra-(trichlorophenyl)-2,3,4,5-tetraethylhexasiloxane. Similarly prepared from 110 g (0.36 mole) trichlorophenylethyldichlorosilane and 23.1 g (0.21 mole) trimethylchlorosilane; yield 71%; n_D^{20} 1.5470; d_4^{20} 1.3435.

Found %: C 39.3, 39.8; H 4.2, 4.3; Si 13.8, 13.65; Cl 36.8, 37.0. $C_{38}H_{46}O_5Si_6Cl_{12}$. Calculated %: C 38.8; H 3.9; Si 14.3; Cl 36.2.

1,3-Hexamethyl-2-phenyl-2-ethyltrisiloxane. Prepared as above from 100 g (0.32 mole) phenylethyldiethoxysilane and 83 g (0.76 mole) trimethylchlorosilane; yield 70%; n_D^{20} 1.4830; d_4^{20} 1.0234.

Found %: C 53.06, 53.30; H 8.63, 8.75; Si 25.90, 26.12. $C_{14}H_{28}O_2Si_3$. Calculated %: C 53.84; H 8.97; Si 26.92.

The viscosity of these organosilicon liquids was determined with the Ostwald capillary viscosimeter. The dielectric permittivity was determined as the ratio of the capacity of the condenser formed by electrodes filled with the substance to the capacity of an air condenser [9].

SUMMARY

1. New liquid (1−n)-hexamethylpolychlorophenylethylsiloxanes containing 1, 2 or 3 chlorine atoms in the phenyl radical and 3 to 6 silicon atoms in the molecule were synthesized.

2. The physicochemical properties were studied and the dielectric permittivity of the new compounds was found to increase with increasing number of chlorine atoms at the phenyl radical and with increasing number of silicon atoms in the molecule.

3. Examination of the viscosity in the 0-120° temperature range showed that the activation energy of viscous flow in all of the (1−n)-hexamethylpolychlorophenylethylsiloxanes is considerably higher than that of the (1−n)-hexamethylpolydimethylsiloxanes. The activation energy of viscous flow rises sharply with increasing number of chlorine atoms at the phenyl radical and rises appreciably with increasing number of silicon atoms in the molecule.

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SYNTHESIS OF 2-CYCLOBUTYLBUTANE AND 3-CYCLOBUTYLPENTANE

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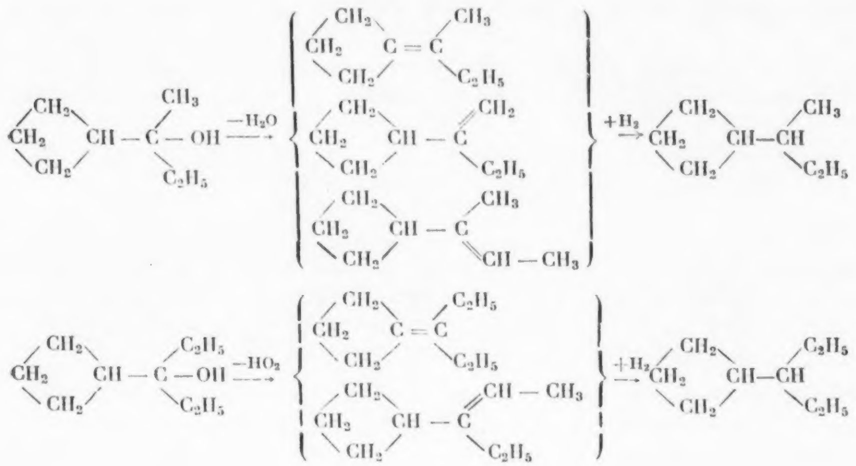
We showed earlier [1] that dehydration of dimethylcyclobutylcarbinol by heating with a few drops of concentrated sulfuric acid leads to good yields of both of the possible cyclobutane hydrocarbons with a double bond in the side chain. Formation of hydrocarbons with a five-membered ring was not observed.

In the present work this method of dehydration was applied to two other tertiary alcohols – methylethylcyclobutyl carbinol and diethylcyclobutyl carbinol. As in the case of dimethylcyclobutyl carbinol, the corresponding cyclobutyl olefins were obtained in yields of over 80%. Contrary to what was achieved in the preceding work [1], we were unable to isolate the pure olefins due to the closeness of their boiling points, and the mixture obtained by dehydration of the carbinol was fractionated in a rectifying column to give fractions only enriched in one or the other of the olefins. Hydrogenation of these fractions (separately), which differed in boiling point, refractive index and specific gravity, led to one and the same saturated hydrocarbon. In this manner the synthesis was effected for the first time of two homologs of cyclobutane: from methylethylcyclobutyl carbinol was obtained 2-cyclobutylbutane; from diethylcyclobutyl carbinol was obtained 3-cyclobutylpentane.



It should be noted that, although we were the first to synthesize these hydrocarbons, their formation has been erroneously reported in a number of handbooks. Obolentsev [2], Doss [3] and Egloff [4], for example, state that 3-cyclobutylpentane is a substance obtained by Kizhner [5] by hydrogenation of the product of dehydration of diethylcyclobutyl carbinol, although (as was later found by the author himself [6]) this substance was actually a mixture of homologs of cyclopentane. Concerning 2-cyclobutylbutane, its structural formula is erroneously given in Obolentsev's handbook for the isobutylcyclobutane synthesized by Kazansky and Golmov [7].

The 2-cyclobutylbutane and 3-cyclobutylpentane described in the present paper can be compared in properties with the isopropylcyclobutane previously described. Comparison of the increments of molecular refractions (Table 1) of these three homologs of cyclobutane with branched side chains shows that with increasing complexity of the chain the value of the increment of the molecular refraction gradually falls.

TABLE 1

Number	Hydrocarbon	Increment of MR_D
1	$CH_2\langle{CH_2 \atop CH_2}\rangle CH-CH(CH_3)_2$	0,48
2	$CH_2\langle{CH_2 \atop CH_2}\rangle CH-CH(CH_3)(C_2H_5)$	0,39
3	$CH_2\langle{CH_2 \atop CH_2}\rangle CH-CH(C_2H_5)_2$	0,21

TABLE 2

Number	Carbinol	Increment of MR_D
1	$CH_2\langle{CH_2 \atop CH_2}\rangle CH-\underset{OH}{C}(CH_3)_2$	0,19
2	$CH_2\langle{CH_2 \atop CH_2}\rangle CH-\underset{OH}{C}(CH_3)(C_2H_5)$	0,04
3	$CH_2\langle{CH_2 \atop CH_2}\rangle CH-\underset{OH}{C}(C_2H_5)_2$	0,01

The same regularity is found on comparing the increments of molecular refractions of the cyclobutyl carbinols that we synthesized (Table 2).

It should be noted that the magnitude of the increment of molecular refraction even for dimethylcyclobutyl carbinol differs considerably from the mean value of the increment (0.47) accepted for cyclobutane derivatives. This depression is evidently due to the influence of the ${R \atop R_1}\!\!>\underset{OH}{C}-$ grouping attached to the ring. A similar phenomenon was observed by Bruylants [8] in the case of tertiary alcohols of the cyclopropane series. In this case the mean increment of molecular refraction was 0.20 instead of 0.70 as accepted for compounds of the cyclopropane series.

EXPERIMENTAL

2-Cyclobutylbutane

1. Methylcyclobutyl ketone. A mixture of 64 g of cyclobutanecaproic acid and twice the volume of glacial acetic acid was passed at 410° at the rate of 16 ml/hr over 50 g freshly reduced manganese dioxide. 42.8 g of ketone was obtained (63.2% of the theoretical, calculated on the cyclobutanecaproic acid taken into reaction); b. p. 134-136° (752 mm); n_D^{20} 1.4320; d_4^{20} 0.9013.

2. Methylethylcyclobutyl carbinol. 42 g (0.43 mole) methylcyclobutyl ketone in an equal volume of dry ether was added in a nitrogen stream (with cooling and stirring) to a Grignard reagent prepared from 109 g (1 mole) ethyl bromide and 25 g (1 g-atom) Mg in 100 ml dry ether. The reaction product was treated in a manner similar to that for the previously described dimethylcyclobutyl carbinol [1]. After the ether had been driven off, the residue was fractionated from a Favorsky flask. The 164-165° (746 mm) fraction was methylethylcyclobutyl carbinol; yield 44.7 g (83% of the theoretical, calculated on the methylcyclobutyl ketone taken into reaction); n_D^{20} 1.4520; d_4^{20} 0.8976; found MR 38.51; calculated for $C_8H_{16}O$ 38.47; increment of MR 0.04.

3. 2-Cyclobutylbutane. 44.1 g methylethylcyclobutyl carbinol was heated with 2 drops of concentrated sulfuric acid in a flask joined to a glass-packed rectifying column. During the dehydration the hydrocarbon was distilled off and was collected together with water in the receiver. The hydrocarbon layer was washed with water, with 10% $NaHCO_3$ solution and again with water, dried over fused $CaCl_2$ and boiled with metallic sodium. Yield 32.4 g hydrocarbon (80.4% of the theoretical, calculated on the methylethylcyclobutyl carbinol taken for the dehydration); b. p. 110-132° (760 mm); n_D^{20} 1.4479; d_4^{20} 0.7956; found MR 37.04; calculated for C_3H_{14} F

TABLE 3

Fraction number	B. p. in °C (760 mm)	Amount in g	n_D^{20}	d_4^{20}
I	112.5—126.0	3.4	1.4371	0.7845
II	126.0—129.1	3.1	1.4453	0.7926
III	129.1—132.1	13.2	1.4504	0.7971
IV	132.1—132.3	5.2	1.4510	0.7988
Total		29.9		

TABLE 4

Fraction number	Amount in g		B. p. in °C (760 mm)	n_D^{20}	d_4^{20}
	taken	obtained			
I*	3.1	1.7	123.0	1.4205	0.7610
II	7.4	6.1	123.0	1.4207	0.7612
III	12.1	10.2	123.0	1.4207	0.7611
IV	4.7	3.7	123.0	1.4206	0.7612

* 26.5 g of silica gel was taken for the chromatographing.

36.48; increment of MR 0.56. 32.2 g of the product of dehydration was fractionated in a copper-packed column with an efficiency of 35 theoretical plates. Results of the fractionation are in Table 3.

Fractions were hydrogenated individually at room temperature over platinized carbon (0.3 g) in a duck of the usual type. Distilled ethyl alcohol (25-30 ml) was used as solvent in all cases. After hydrogenation, the hydrocarbon was distilled off with steam, separated from the water, chromatographically purified in a silica gel column (40-45 g silica gel) and distilled. Results are presented in Table 4.

21 g of a mixture of four hydrogenated fractions was distilled in a column packed with copper and with an efficiency of 33 theoretical plates.

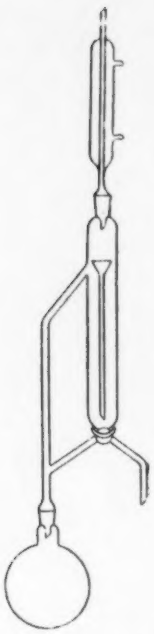
2-Cyclobutylbutane has b. p. 123° (760 mm); n_D^{20} 1.4207; d_4^{20} 0.7612; found MR 37.33; calculated for C_8H_{16} 36.94; increment of MR 0.39.

Found %: C 85.68, 85.60; H 14.38, 14.47. C_8H_{16}. Calculated %: C 85.62; H 14.38.

3-Cyclobutylpentane

1. Ethyl cyclobutanecaproate. 100 g (1 mole) cyclobutanecaproic acid, 250 ml ethyl alcohol; 150 ml benzene and 5 ml concentrated sulfuric acid were boiled in the apparatus illustrated in the figure; water distilled off at the same time as part of a ternary azeotrope with ethyl alcohol and benzene which separated into two layers in the separator. The lower layer (aqueous alcohol) was progressively run off as it accumulated; the top layer (alcohol-benzene) was returned to the flask. At the end of the reaction, the benzene was distilled off in the form of an azeotrope with alcohol. The residue was cooled, poured into water, neutralized with sodium carbonate, washed with water, dried over magnesium sulfate and dist lled from a Favorsky flask. 124 g (97% of the theoretical, calculated on the acid taken) of ethyl cyclobutanecaproate was obtained; b. p. 147.5-149° (746 mm); n_D^{20} 1.4263; d_4^{20} 0.9549; found MR 34.39; calculated for $C_7H_{12}O_2$ MR 33.86; increment of MR 0.53.

2. Diethylcyclobutyl carbinol. 64 g (0.5 mole) ethyl cyclobutanecaproate in an equal volume of dry ether was poured in a nitrogen stream (with stirring) into a Grignard reagent prepared from 163.5 g (1.5 moles) ethyl bromide and 36.5 g (1.48 g-atoms) Mg in 250 ml dry ether (the temperature of the reaction mixture rose to 63°



during the operation). The reaction mixture was kept at 40° for 5 hours and left overnight; the reaction product was then worked up in the same manner as for the synthesis of dimethylcyclobutyl carbinol [1]. After removal of the ether, the residue was fractionated in vacuum from a Favorsky flask. Fractions with b. p. 85-85.6° (22 mm) and 187-188° (756 mm) were diethylcyclobutyl carbinol. Yield 66.4 g (92.6% of the theoretical, calculated on the ethyl ester taken into reaction); n_D^{20} 1.4567; d_4^{20} 0.9001; found MR 42.98; calculated for $C_9H_{18}O$ MR 43.08.

3. 3-Cyclobutylpentane. Dehydration of diethylcyclobutyl carbinol and further working-up of the product of dehydration were effected as described for methylethyl cyclobutyl carbinol. The reaction gave (after boiling with metallic sodium) 44.8 g of hydrocarbon (88% of the theoretical, calculated on diethylcyclobutyl carbinol taken

TABLE 5

Fraction number	B. p. in °C (760 mm)	Amount in g	n_D^{20}	d_4^{20}
I	146.0—153.0	4.8	1.4502	
II	153.0—153.8	12.2	1.4532	0.8080
III	153.8—154.2	11.8	1.4552	0.8097
IV	154.2—155.4	12.9	1.4582	0.8109

for dehydration – 58.4 g); b. p. 146-155° (760 mm); n_D^{20} 1.4544; d_4^{20} 0.8075; found MR 41.66; calculated for C_9H_{16} F MR 41.09; increment of MR 0.57. 44.6 g of the product of dehydration was fractionated in a copper-packed column with an efficiency of 60 theoretical plates (Table 5).

Hydrogenation of fractions, separation and purification of the products of hydrogenation were effected as for the synthesis of 2-cyclobutylbutane. Results are presented in Table 6.

TABLE 6

Fraction number	Amount in g		B. p. in °C (760 mm)	n_D^{20}	d_4^{20}
	taken	obtained			
I	4.5	2.3	148.7	1.4306	0.7813
II	11.9	10.2	148.7	1.4308	0.7814
III	11.5	10.2	148.7	1.4308	0.7815
IV	12.5	11.1	148.7	1.4308	0.7813

33 g of a mixture of all of the four hydrogenated fractions was distilled in a copper-packed column with an efficiency of 40 theoretical plates.

3-Cyclobutylpentane has b. p. 148.7° (760 mm); n_D^{20} 1.4308; d_4^{20} 0.7815; found MR 41.77; calculated for C_9H_{18} MR 41.56; increment of MR 0.21.

Found %: C 85.73, 85.69; H 14.33, 14.43. C_9H_{18}. Calculated %: C 85.62; H 14.38.

SUMMARY

1. Dehydration of methylethyl- and diethylcyclobutyl carbinol by heating with a few drops of concentrated sulfuric acid takes place with retention of the four-membered ring.

2. Two cyclobutane hydrocarbons were prepared for the first time: 2-cyclobutylbutane and 3-cyclobutylpentane.

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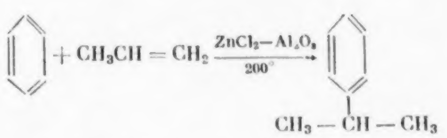
CATALYTIC ALKYLATION OF BENZENE WITH ALKENES IN THE VAPOR PHASE

I. THE ALKYLATION OF BENZENE WITH PROPYLENE

N. I. Shuikin and N. A. Pozdnyak

In our previous work in collaboration with Kuchkarev [1, 2] it was shown that zinc chloride deposited on alumina is an active catalyst for alkylations of benzene with oxygen-containing compounds (alcohols and ethers) in the vapor phase. Later we employed this catalyst in alkylations of benzene with alkenes. We studied the alkylation of benzene with propylene which were brought into contact with zinc chloride on alumina or silica at atmospheric and higher pressures (2 to 20 atmos).

In this work we found that at 300° and atmospheric pressure (space velocity 0.15 hour^{-1} and a benzene/propylene molar ratio of 2:1) the yield of a broad isopropylbenzene fraction with b. p. 150-160°* reaches 52.5%, calculated on the propylene charged into the reaction. At 200° and 5 atmos (space velocity 0.45 hr^{-1}, benzene/propylene molar ratio of 4:1 to 6:1) the yield of isopropylbenzene (b. p. 152-153°) was 50%, reckoned on the propylene introduced into the reaction and 75.5% on the reacted propylene. This alkylate contained 13% isopropylbenzene and 6.7% diisopropylbenzenes:



$$C_6H_6 + 2CH_3CH = CH_2 \rightarrow o\text{-},\ m\text{-}\ и\ p\text{-}C_6H_4(C_3H_7)_2$$

EXPERIMENTAL

Alkylation of benzene with propylene at atmospheric pressure. Benzene was alkylated with propylene in an apparatus of the usual flow type. The optimum temperature for this reaction was found to be 300° (Fig. 1). Increase of space velocity to above 0.2 hr^{-1} (Table 1) and increase of the excess of benzene to correspond to a benzene/propylene molar ratio of 4:1 leads to appreciable fall in yield of the isopropylbenzene fraction (Table 2, experiments 2 and 3; 4 and 5).

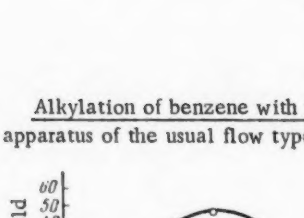


Fig. 1. Influence of temperature on yield of isopropylbenzene fraction in % of the original propylene (benzene//propylene molar ratio of 2:1, space velocity 0.15 hr^{-1}).

Nine specimens of catalysts with different zinc chloride contents were investigated in benzene alkylation experiments. Results are presented in Table 2.

The experiments in this series were performed at 300° and a space velocity of 0.15 hr^{-1}. 26 g of benzene was taken in each experiment.

* The 150-160° fraction contained 75% of isopropylbenzene.

TABLE 1

Effect of Space Velocity on Yield of Isopropylbenzene Fraction with b. p. 150-160°
(temperature 300°, benzene/propylene molar ratio of 2:1)

Space velocity in hr^{-1}	Yield of isopropylbenzene fraction in % of propylene taken
0.1	49.3
0.15	50.1
0.2	49.5
0.3	41.4

We see from the data of Table 2 that a drop of the zinc chloride content of the catalyst to below 15% leads to a sharp fall in activity of the catalyst. Zinc chloride deposited on silica was found to be a less active catalyst. Alumina that had previously been treated with hydrogen chloride did not exhibit activity in the alkylation of benzene with propylene.

In this manner conditions were established for the alkylation of benzene with propylene (temperature 300°, space velocity 0.15-0.2 hr^{-1}, benzene/propylene molar ratio of 2:1) which enabled a yield of isopropylbenzene fraction (b. p. 150-160°) of 52.5% to be obtained, calculated on the propylene charged. In this case the catalyzate contained 30% of isopropylbenzene fraction.

TABLE 2

Alkylation of Benzene with Propylene Over Catalysts
(benzene/propylene molar ratio = 2:1; in expts. 3 and 5 the ratio is 4:1)

Experiment no.	Catalyst	Yield of isopropylbenzene fraction (b.p. 150-160°)		Yield of fraction with b. p. above 160°, in g
		in % of catalyzate	in % of theore. on propylene	
1	40% $ZnCl_2$ on Al_2O_3	28.6	50.0	1.5
2	30% ditto	30.0	52.5	2.5
3	30% "	14.5	45.0	1.5
4	20% "	27.0	45.0	1.0
5	20% "	16.1	50.0	1.0
6	15% "	30.6	47.5	1.5
7	10% "	10.0	15.0	1.3
8	8% "	4.6	6.5	1.0
9	30% $ZnCl_2$ on SiO_2	16.1	25.0	1.5
10	20% $ZnCl_2$ on SiO_2	23.0	30.0	1.5
11	Al_2O_3 + HCl	—	—	1.5

We carried out alkylations of benzene with propylene diluted with nitrogen under the optimum conditions established. Results of a typical experiment are given below. 39 g (0.5 mole) of benzene was passed over a catalyst consisting of 30% zinc chloride and 70% alumina for 2 hours with simultaneous passage of propylene diluted with nitrogen with a velocity of 70 ml/min (propylene content of the mixture 57%). This experiment gave 39 g of liquid catalyzate and 6.5 liters of gas containing 23% of saturated hydrocarbons. Distillation of the catalyzate in a column with an efficiency of 20 theoretical plates gave the fractions whose properties are listed in Table 3.

The yield of isopropylbenzene with b. p. 152-153°, n_D^{20} 1.4930 and d_4^{20} 0.8625 is 33.2% of theory, calculated on the propylene introduced, and 46.7% on the reacted propylene. The catalyzate in this case contained 22.2% isopropylbenzene and 6.6% dialkylbenzenes.

Alkylation of benzene with propylene at higher pressures. An apparatus of the flow type was used [3]. A mixture of propylene and acetone from a cylinder was pressed into the reactor via a flowmeter. The effect of composition of the gas mixture on yield of isopropylbenzenes was studied at 200° and 20 atmos and with a benzene/propylene molar ratio of 7:1 (Table 4).

TABLE 3

Fractional Distillation of Catalyzate

Fraction no.	B. p. in °C	% of catalyzate	n_D^{20}
I	До 80	0.8	1.4550
II	80—85	66.5	1.5000
III	85—152	3.9	1.4930
IV	152—153	21.4	1.4930
V	153—155	0.8	1.4928
VI	Above 155	6.6	1.5010

TABLE 4

Effect of Composition of Gas Mixture on Yield of Isopropylbenzene Fraction

Volume % of propylene in mixture	% yield of isopropylbenzene fraction with b.p. 150-160°	
	On propylene taken	On propylene reacted
16	40	66
18	38	61
20	41	65
23	41	64

TABLE 5

Influence of Temperature on Yield of Isopropylbenzene Fraction

Experiment number	Temperature in °C	% composition of catalyzate		Yield of isopropylbenzene fraction in % of theoretical, calculated on reacted propylene
		of isopropylbenzene fraction with b. p. 150-160°	of fraction with b.p. > 160°	
1	250	22.0	6.0	44.0
2	200	20.4	7.0	75.0
3	180	16.5	5.4	50.0

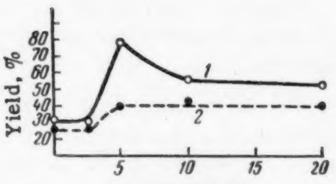


Fig. 2. Influence of pressure on the yield of isopropylbenzene fraction with b. p. 150-160° (temperature 200°, space velocity 0.45 hr^{-1}, benzene/propylene molar ratio 8:1): 1) yield of isopropylbenzene fraction calculated on the reacted propylene; 2) yield of isopropylbenzene fraction based on propylene introduced.

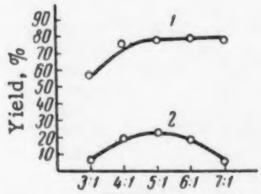


Fig. 3. Influence of benzene/propylene molar ratios on yield of isopropylbenzene fraction with b. p. 150-160° (pressure 5 atmos): 1) yield of isopropylbenzene fraction based on reacted propylene; 2) % content of isopropylbenzene fraction in catalyzate.

It is evident from the data of Table 4 that increase of the propylene content of the gas mixture from 16 to 23% has no marked influence on the yield of the isopropylbenzene fraction. With the objective of determining the influence of temperature on the yield of this fraction, experiments were run at a pressure of 20 atmos with a benzene/propylene molar ratio of 5:1 and a catalyst containing 30% of zinc chloride. Benzene was alkylated with a mixture of propylene and nitrogen containing 15% propylene (Table 5).

At pressures in the range of 5 to 20 atmos the yield of isopropylbenzene (calculated on the propylene introduced) remains constant, but the yield calculated on the reacted benzene increases with falling pressure and reaches a maximum of 78% at 5 atmos (Fig. 2).

Alkylation experiments using various molar benzene/propylene ratios were carried out at 200° with a space velocity of 0.45 hr^{-1} and pressures of 5, 10 and 20 atmos with a mixture containing 20% of propylene (Table 6).

TABLE 6

Influence of Benzene/Propylene Molar Ratio on Yield of Alkylbenzenes (temperature 200°, space velocity 0.45 hr^{-1}, mixture containing 20% of propylene)

Pressure in atmos	Benzene/propylene molar ratio	% content in catalyzate		% yield	
		of isopropylbenzene fraction, b.p. 150-160°	of fraction with b. p. above 160°	based on propylene introduced	on reacted propylene
5	7 : 1	6.0	2.0	55.1	78.0
5	6 : 1	18.0	8.0	43.2	77.1
5	5 : 1	21.1	10.3	50.5	76.0
5	4 : 1	20.0	13.0	55.0	75.2
5	3 : 1	7.0	3.5	51.0	60.1
10	7 : 1	7.0	4.0	40.5	56.0
10	6 : 1	8.0	8.8	50.1	60.2
10	5 : 1	8.1	9.2	30.2	43.1
20	10 : 1	6.5	1.5	55.0	92.1
20	7 : 1	7.3	4.4	40.1	66.0
20	5 : 1	8.5	9.5	30.3	33.0

TABLE 7

Fractional Distillation of Catalyzate

Fraction number	B. p. in °C	% content on catalyzate	n_D^{20}
I	79-80	79.7	1.5000
II	80-110		1.4895
III	110-120	0.7	1.4595
IV	120-147		1.4670
V	147-152		1.4900
VI	152-153	12.9	1.4912
VII	153-164		1.4900
VIII*	164-207	6.7	
IX	Residue		

* This fraction was distilled from the flask fitted with a still head.

These results indicate that with increasing excess of benzene in the reaction mass, the yield of isopropylbenzene fraction, based on reacted propylene and with a benzene/propylene molar ratio of 10 : 1, reaches 92%, although in this event the catalyzate only contains 6.5% of isopropylbenzene fraction.

The relation between the benzene/propylene molar ratio and the yield of isopropylbenzene fraction is illustrated by curves 1 and 2 in Fig. 3.

The conclusion to be drawn from Fig. 3 is that benzene/propylene molar ratios within the range of 4 : 1 to 6 : 1 are the optimum for the reaction. Results of a typical experiment under the optimum conditions established are as follows: the amount of benzene taken was 312 g (4 moles), and 15 liters propylene were introduced. Reaction gave 320 g of catalyzate (with n_D^{20} 1.4970) and 5 liters of propylene (calculated as 100%). The catalyzate was dried with calcium chloride and distilled over metallic sodium at 752 mm in a column with an efficiency of 20 theoretical plates (Table 7).

Fraction I (b. p. 79-80°) was unreacted benzene. Fractions boiling in the 80-147° range were refractionated under the same conditions to give a fraction with b. p. 80-95° and n_D^{20} 1.4680; this contained 73% of aromatics; the unsulfonatable residue had n_D^{20} 1.4105. Another fraction of the redistillate had b. p. 95-130° and n_D^{20} 1.4350; it contained 45% of aromatic hydrocarbons and 55% of unsulfonatable residue with n_D^{20} 1.4105. A fraction with b. p. 152-153° was pure isopropylbenzene with n_D^{20} 1.4912 and d_4^{20} 0.8620; its yield was 50%, calculated on the propylene introduced, and 75.5% on the reacted propylene. Raman spectrographic examination of fraction VIII (b. p. 164-207°) showed it to be a mixture of diisopropylbenzenes with alkyl groups in the 1,2-, 1,3- and 1,4-positions.

SUMMARY

1. Alumina-supported zinc chloride catalyzes the alkylation of benzene with propylene.

2. Conditions were established for obtaining a 50% a yield of pure isopropylbenzene, calculated on the propylene introduced into reaction, and 75% on the reacted propylene.

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OXIDATION-REDUCTION SYSTEMS FOR INITIATION OF RADICAL PROCESSES

4. OXIDATION-REDUCTION SYSTEMS FOR INITIATION OF POLYMERIZATIONS IN HYDROCARBON MEDIA

E. I. Tinyakova, B. A. Dolgoplosk and M. B. Rabinovich

Reversible Systems

Oxidation-reduction systems are an active source of free radicals in emulsion polymerization processes; under certain conditions they can also be used for initiation of polymerization in homogeneous hydrocarbon medium.

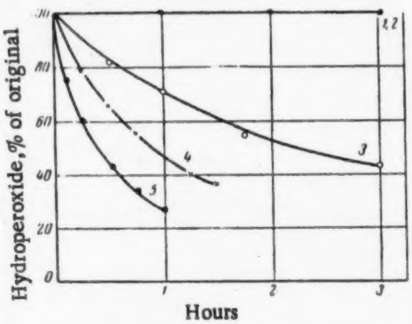

Fig. 1. Kinetics of reaction of isopropylbenzene hydroperoxide with benzoin in presence of ferric naphthenate: 1) hydroperoxide + benzoin, 60°; 2) hydroperoxide + Fe^{3+} naphthenate, 60°; 3,4,5) hydroperoxide + benzoin + naphthenate at 40, 50 and 60°, respectively.

Many investigators observed a considerable rise in rate of polymerization of olefins in a homogeneous medium on introduction into the system, in addition to benzoyl peroxide, of some compounds possessing reducing properties (sulfinic acids, amines, hydroxycarbonyl compounds, etc.) [1, 2]. Kern showed that systems of iron, lead or other metal naphthenates, benzoin and benzoyl peroxide were considerably more active in polymerization of olefins than benzoyl peroxide alone [1].

Kern advances the hypothesis that the accelerating effect of metal salts is the result of initiation of a cycle of reversible oxidation-reduction transformations.

$$Fe^{++} \underset{\text{reducing agent}}{\overset{\text{peroxide}}{\underset{2}{\overset{1}{\rightleftharpoons}}}} Fe^{+++} + \text{radicals}$$

Kern, however, did not produce any experimental evidence of these transformations. The efficiency of action of such a system is evidently governed by reaction 2 since reaction 1 takes place almost instantaneously in hydrocarbon media. It was therefore to be expected that replacement of benzoin by compounds with more strongly reducing properties (especially dienols) should lead to increased activity of the system as an initiator of polymerization. In experiments with dihydroxymaleic acid we had previously demonstrated the possibility of employing such systems for initiation of polymerization in aqueous emulsions at temperatures down to −50° [3].

The present communication is concerned with a study of the activity and the mechanism of action of reversible oxidation-reduction systems in hydrocarbon media when employing the diethyl ester of dihydroxymaleic acid and benzoin as reducing agents; it also deals with initiation of styrene polymerization under the influence of isopropylbenzene hydroperoxide and salts of metals of variable valence.

a) Kinetics of reaction of peroxides with reducing agents. The kinetics of consumption of isopropylbenzene hydroperoxide during its reaction with benzoin in ethylbenzene solution at various temperatures in presence of ferric naphthenate are plotted in Fig. 1. The concentration of hydroperoxide and reducing agent was 0.02 mole/liter, and that of ferric naphthenate 0.002 mole/liter.

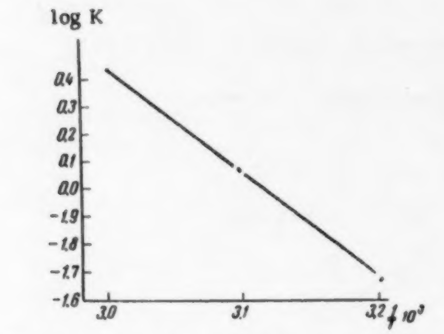

Fig. 2. Temperature dependence of the velocity constant of the reaction of isopropylbenzene hydroperoxide with benzoin in presence of ferric naphthenate.

The plots show that in the temperature region up to 60°, isopropylbenzene hydroperoxide does not react with benzoin or ferric naphthenate (curves 1 and 2). An accelerating influence of ferric iron salts on the breakdown of isopropylbenzene hydroperoxide does not develop to an appreciable extent until a temperature of 100° is reached. A reaction between isopropylbenzene hydroperoxide and benzoin at 20-60° only takes place in presence of ferric naphthenate and is satisfactorily represented by a second-order equation (Table 1).

The over-all energy of activation of this reaction is 18 kcal/mole (Fig. 2).

Due to the strong reducing properties of the ester of dihydroxymaleic acid, the peroxide is decomposed in its presence at a much higher speed than in presence of benzoin (Fig. 3).

TABLE 1

Kinetics of Reaction of Isopropylbenzene Hydroperoxide with Benzoin in Presence of Ferric Naphthenate in Ethylbenzene Solution

40°			50°			60°		
Duration in min	% of unreacted hydroperoxide	K_2	Duration in min	% of unreacted peroxide	K_2	Duration in min	% of unreacted peroxide	K_2
30	81.5	0.401	14	78.8	0.984	15	60.0	2.28
60	70.5	0.393	29	65.5	0.933	30	42.1	2.37
90	60.8	0.395	44	55.5	0.960	45	34.3	2.21
120	53.4	0.410	60	47.8	0.932	60	27.2	2.31
180	42.5	0.409	90	35.2	1.043			
	Mean	0.402		Mean	0.984		Mean	2.29

b) Reduction of ferric naphthenate with benzoin and diethyl dihydroxymaleate. The kinetics of reduction of the ferric to the ferrous salt were studied in toluene or ethylbenzene solution. The over-all reaction equation is:

$$2Fe^{3+}(OCOR)_3 + \underset{\textstyle OH}{\underset{|}{-CH}}-\underset{\textstyle O}{\underset{\|}{C}}- \rightarrow 2Fe^{2+}(OCOR)_2 + \underset{\textstyle O}{\underset{\|}{-C}}-\underset{\textstyle O}{\underset{\|}{C}}- + 2RCOOH.$$

The process was characterized by the rate of formation of Fe^{2+} naphthenate as determined by titration with 0.1 N $K_2Cr_2O_7$ after transfer of the iron salts to the aqueous phase (shaking with 1:1 sulfuric acid). The experimental results are plotted in Fig. 4.

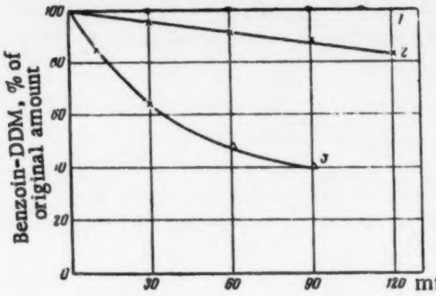

Fig. 3. Kinetics of reaction of benzoyl peroxide (BP) with benzoin and diethyl dihydroxymaleate (DDM) in solution in presence of ferric naphthenate: 1) BP + ferric naphthenate, 50°; 2) BP + benzoin + ferric naphthenate, 25°; 3) BP + DDM + + ferric naphthenate, 20°.

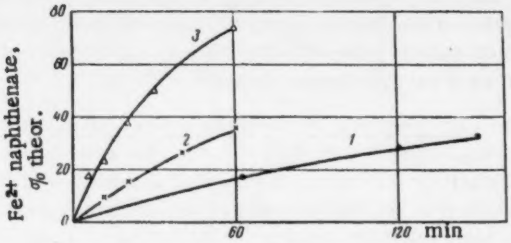

Fig. 4. Kinetics of reduction of ferric naphthenate with benzoin in ethylbenzene solution: 1) 20°; 2) 30°; 3) 40°.

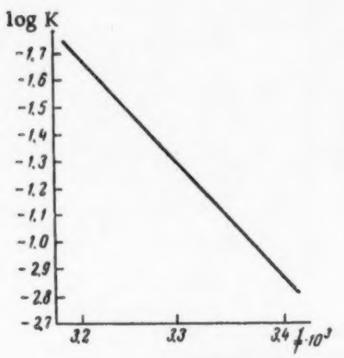

Fig. 5. Temperature dependence of the velocity constant of reduction of ferric to ferrous iron by benzoin in ethylbenzene solution.

Reduction of ferric naphthenate with benzoin goes (slowly) even at 20°. The reaction is satisfactorily described by a second-order equation (Table 2). The over-all energy of activation of the process is 19.7 kcal/ /mole (Fig. 5).

Reduction of ferric to ferrous naphthenate by diethyl dihydroxymaleate is a very much faster process (the yield of ferrous naphthenate at 20° after 10 minutes is 70% of the theoretical). The reaction evidently starts with formation of a complex as manifested by development of the violet-blue color characteristic of the complex of Fe^{3+} with dihydroxymaleic acid or its ester [4].

c) Mechanism of action of the system. Results of a study of the kinetics of the individual reactions leads to the conclusion that the process is realized by a type of reversible systems [1, 3] in which the iron salts function as electron carriers. Experiments show that the oxidation of ferrous naphthenate by isopropylbenzene hydroperoxide and by benzoyl peroxide goes substantially instantaneously even at a temperature of −70°. The over-all reaction velocity is governed by the reduction reaction $Fe^{3+} \rightarrow Fe^{2+}$ as is also indicated by the similarity

TABLE 2

Kinetics of Reduction of Ferric Naphthenate with Benzoin in Ethylbenzene Solution
$c_a = c_{benzoin} = 0.0147$ mole/liter; $c_{Fe^{3+} naphth.} = 0.0441$ mole/liter

20°			30°			40°		
time, min	$c_a - c_x$	K_2	time, min	$c_a - c_x$	K_2	time, min	$c_a - c_x$	K_2
62	0.0122	0.068	11	0.0134	0.185	7	0.0123	0.58
120	0.0106	0.064	20	0.0124	0.195	11	0.0113	0.56
150	0.0098	0.065	40	0.0108	0.185	20	0.0090	0.59
225	0.0081	0.065	60	0.0094	0.180	30	0.0072	0.59
						60		
	Mean	0.066		Mean	0.186		Mean	0.58

between the values of the energy of activation of the reduction $Fe^{3+} \rightarrow Fe^{2+}$ and of the over-all energy of activation of the reaction of the hydroperoxide with benzoin in presence of Fe^{3+} naphthenate. It is thus demonstrated that the general laws previously established for systems of the type in question in aqueous media [3] are also valid for hydrocarbon media.

d) Employment of reversible systems for initiation of polymerization of styrene. Data for the kinetics of polymerization of styrene at 50° under the influence of a reversible system with participation of diethyl dihydroxymaleate are plotted in Fig. 6. The results show the existence of a direct relation between kinetics of interaction of the components and the kinetics of polymerization. Thus, the polymerization process goes with very low velocity if the system contains only isopropylbenzene hydroperoxide or hydroperoxide and naphthenate

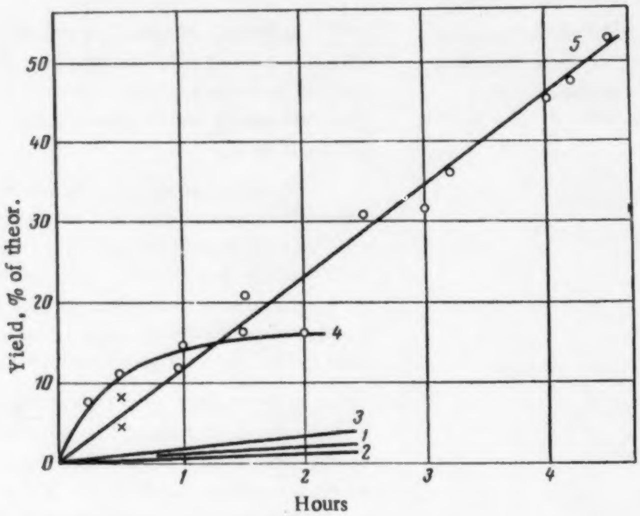

Fig. 6. Polymerization of styrene in presence of isopropylbenzene hydroperoxide (HP), diethyl dihydroxymaleate (DDM) and ferric naphthenate at 50°: 1) HP; 2) HP + ferric naphthenate; 3) HP + DDM (50 mole% to HP); 4) HP + DDM (50 mole% to HP) + ferric naphthenate (10 mole% to HP); 5) HP + DDM (100 mole% to HP) + ferric naphthenate (100 mole% with continuous introduction of HP).

or hydroperoxide and diethyl dihydroxymaleate (curves 1 to 3). In presence of all three components, however, the necessary conditions are created for the action of the system, and polymerization takes place with considerable speed (curve 4). When one of the components is introduced continuously during the reaction, the polymerization can be carried out with constant velocity, and after 4 hours at 50° the yield of polystyrene is 44% (curve 5).

Breakdown of Hydroperoxide Under the Influence of Salts of Metals of Variable Valence and Utilization of This Reaction for Initiation of Polymerization

Thermal breakdown of isopropylbenzene hydroperoxide takes place with appreciable velocity in inert solvents only at a temperature of about 150°. In a medium of olefins the decomposition takes place at lower temperatures [5]. Marked speeding-up of decomposition is observed in presence of metallic salts at a temperature of 70° and higher. With the objective of utilizing a reaction of this type for initiation of polymerization, we studied the kinetics of breakdown of isopropylbenzene hydroperoxide in styrene solution under the influence of various hydrocarbon-soluble metallic salts of variable valence, as well as the kinetics of polymerization at 70°. The concentration of hydroperoxide was $6.6 \cdot 10^{-2}$ mole/liter, the amount of metallic naphthenate was varied within the range of $6.6 \cdot 10^{-2}$ to $6.6 \cdot 10^{-6}$ mole/liter (from 0.01 to 100 mole% relative to the hydroperoxide). The kinetic curves of polymerization of styrene in presence of hydroperoxide and palladium naphthenate are plotted in Fig. 7. Introduction of traces of palladium naphthenate leads to a marked increase in the velocity of the reaction.

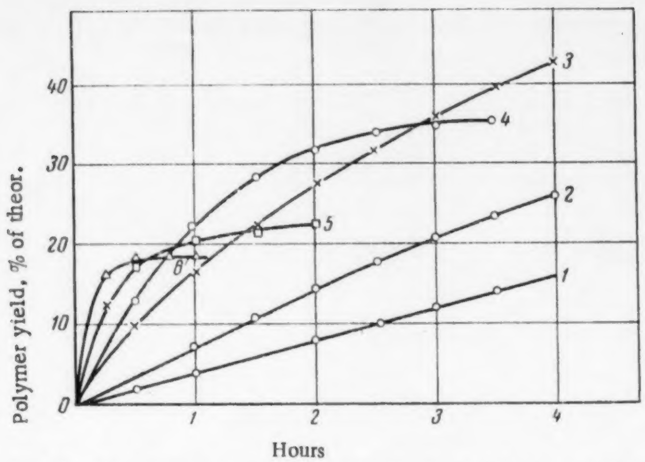

Fig. 7. Influence of palladium naphthenate on the kinetics of styrene polymerization at 70°: 1) without metal; 2-6) with addition of Pd naphthenate (in mole% relative to the hydroperoxide); 2) 0.1, 3) 0.5, 4) 1.0, 5) 5.0, 6) 10.0 mole%.

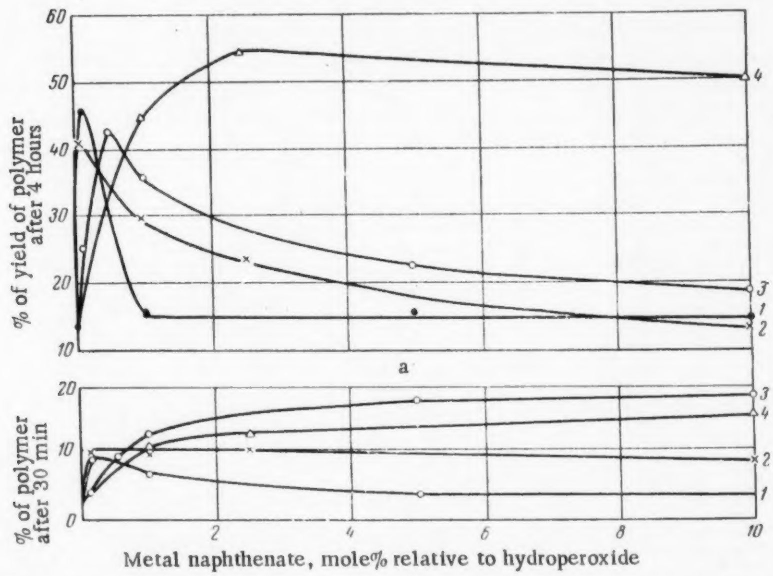

Fig. 8. Influence of concentration of metallic naphthenates on polymer yield during polymerization in presence of isopropylbenzene hydroperoxide at 70°: 1) cobalt naphthenate; 2) copper naphthenate; 3) palladium naphthenate; 4) manganese naphthenate.

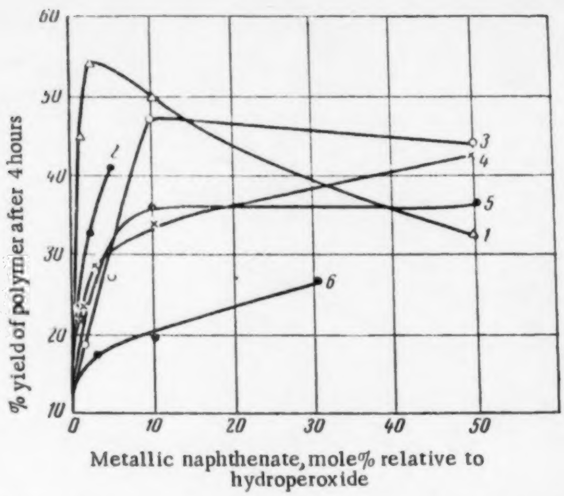

Fig. 9. Influence of concentration of naphthenates on yield of polymer in polymerization of styrene in presence of isopropylbenzene hydroperoxide at 70°: 1) manganese naphthenate; 2) lead naphthenate; 3) silver naphthenate; 4) chromium naphthenate; 5) nickel naphthenate; 6) iron naphthenate.

Similar results were obtained with other metals. Figures 8 and 9 are plots of polystyrene yields (after 30 minutes and 4 hours) versus concentration of naphthenate added. In the cases of copper, cobalt and palladium naphthenates the curve has a well-marked maximum in the region of very low concentrations. The most active concentration of these metals is 0.1-0.5 mole% in relation to hydroperoxide (Fig. 8). When their concentrations exceed the optimum the polymerization goes at high speed in the first instant (Fig. 8, a) but then stops altogether (Fig. 8, b). The active concentrations of manganese, silver and lead naphthenates are somewhat higher (2.5-10 mole% in relation to the hydroperoxide). The curve of polymer yield as a function of concentration of manganese and silver naphthenates likewise passes through a maximum (Fig. 9). The least activity in this system

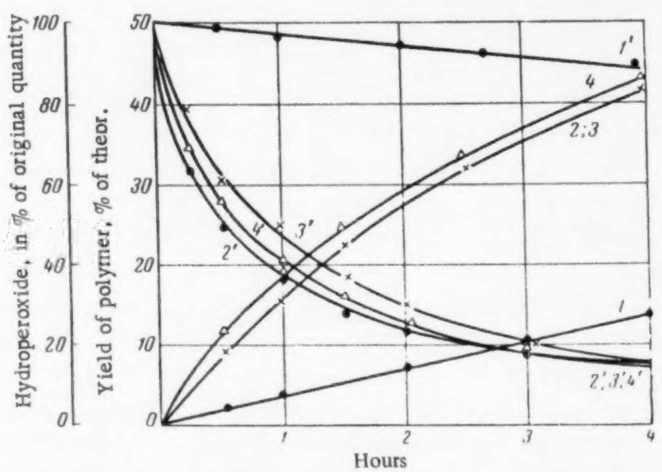

Fig. 10. Kinetics of polymerization of styrene (1, 2, 3 and 4) and kinetics of breakdown of isopropylbenzene hydroperoxide (1', 2', 3' and 4') in presence of metallic naphthenates at 70°: 1, 1') without metal; 2, 2') 0.1 mole% copper naphthenate; 3, 3') 0.1 mole% cobalt naphthenate; 4, 4') 10 mole% manganese naphthenate.

is manifested by naphthenates of iron, nickel and chromium, the most active concentrations of which are considerably higher than in the previously considered cases, amounting to 50-100 mole% relative to the hydroperoxide.

On the basis of the data obtained, metallic naphthenates can be arranged in the following order in respect to their polymerization activity:

$$Co > Cu > Pd > Mn > Pb > Ag > Cr > Ni > Fe.$$

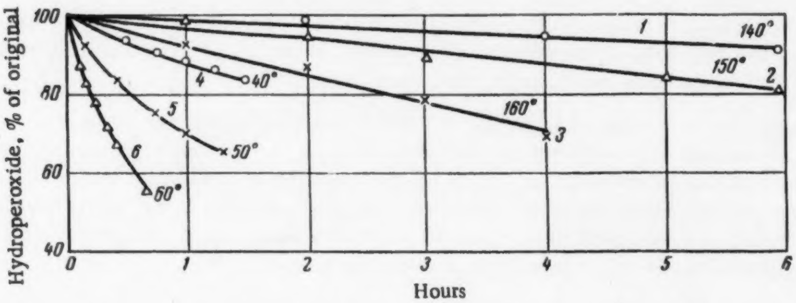

Fig. 11. Kinetics of decomposition of isopropylbenzene hydroperoxide in ethylbenzene: 1, 2 and 3) without metal; 4, 5 and 6) 0.5 mole% cobalt naphthenate.

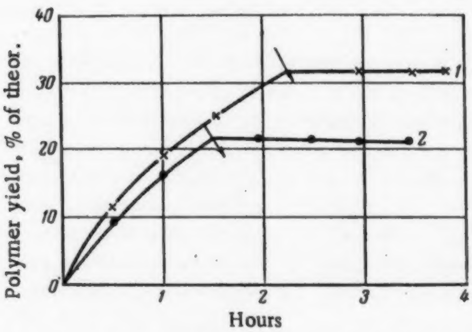

Fig. 12. Influence of benzoquinone on polymerization of styrene at 70° in presence of isopropylbenzene hydroperoxide (HP): 1) HP + 10 mole% Mn naphthenate; 2) HP + 0.1 mole% Cu naphthenate (the arrows indicate the instant of introduction of benzoquinone).

The accelerating effect of metallic salts on the polymerization of styrene in a homogeneous medium is associated with acceleration of breakdown of hydroperoxide, as was shown for naphthenates of copper, manganese and cobalt in the optimum concentrations for the polymerization reaction (Fig. 10). We can detect a very definite relation between the kinetics of breakdown of hydroperoxide under the influence of metallic salts and the kinetics of polymerization.

These data throw light on the cause of the fall in yields of polymer with increase in the quantity of metallic naphthenate to above the optimum. In such cases there is a too rapid unproductive breakdown of hydroperoxide. For example, when using palladium naphthenate in the proportion of 10 mole% (in relation to the hydroperoxide), the polymerization reaction, which started at high speed, almost completely ceased after 15-20 minutes on attaining a yield of polymer of 18% of the theoretical (Fig. 7). Stoppage of polymerization, as shown by analytical data, was associated with the complete absence of peroxide from the system.

Metallic naphthenates appreciably lower the energy of activation of breakdown of hydroperoxide. The kinetics of thermal breakdown of isopropylbenzene peroxide in ethylbenzene solution are plotted in Fig. 11. Heating was carried out at 140, 150 and 160° in the absence of metal and at 60, 70 and 80° in presence of cobalt naphthenate (0.5 mole% in relation to the hydroperoxide). The over-all activation energy of the thermal decomposition of the hydroperoxide is 28.0 kcal/mole; in presence of cobalt naphthenate it falls to 20.1 kcal/mole.

Benzoquinone is known to quantitatively react with free radicals, thereby inhibiting the progress of a chain reaction [6]. As shown in Fig. 12, the introduction of benzoquinone at a certain stage in the process leads to complete stoppage of polymerization.

It follows from the foregoing data that 1 mole of copper naphthenate or palladium naphthenate causes breakdown of about 1000 moles and more of hydroperoxide. Manganese salts exert a similar influence. The absence of stoichiometric ratios for the hydroperoxide decomposition reaction is characteristic also of other, less active, metals. This may be explained on the basis of the hypothesis that decomposition is a reversible process in which hydroperoxide alternately functions as reducing agent and oxidizing agent:

a) $Me^{3+} + ROOH \rightarrow Me^{2+} + RO_2 + H^+$ (with low velocity)

b) $Me^{2+} + ROOH \rightarrow Me^{3+} + RO^{\cdot} + OH^-$ (with very high velocity).

Depending upon the character of the metal employed, the reaction can start either from the stage of oxidation of the -ous form of the metal to the -ic form (for instance, in the case of cobalt) or from the stage of reduction of the -ic form to the -ous form (copper, iron, etc.).

A reaction of type a) was demonstrated by Manchot [7] for the case of hydrogen peroxide with iron salts in aqueous media. In respect to reductive properties hydroperoxides appear to occupy a position intermediate between hydrogen peroxide and organic peroxides. The reductive properties of hydroperoxides are illustrated by their susceptibility under specific conditions to breakdown with loss of oxygen [5]. In the case of benzoyl peroxide, 10 mole% of iron naphthenate has no effect at all on the kinetics of breakdown at 70°, while copper naphthenate under the same conditions has only a very slight accelerating action.

EXPERIMENTAL

Isopropylbenzene hydroperoxide was purified via the sodium salt [8]; after vacuum distillation its concentration was 99.8%. Benzoyl peroxide was recrystallized from a mixture of chloroform and methanol and had a purity of 99.5%. Benzoin was recrystallized from ethanol. Diethyl dihydroxymaleate was prepared from dihydroxymaleic acid [4]. Metal naphthenates were prepared from naphthenic acids with a molecular weight of 203-220.

Due to the very high rate of oxidation of ferrous naphthenate by oxygen, the kinetics of reduction of ferric to ferrous naphthenate by benzoin and diethyl dihydroxymaleate were studied in an atmosphere of pure nitrogen in special ampoules fitted with a side tube and tap. The weighed amount of reducing agent was introduced into the side tube, after which the ampoule was thoroughly purged with oxygen-free nitrogen (three evacuations followed by filling with nitrogen). Iron naphthenate solution was then charged in against a nitrogen back-pressure, the side tube was sealed off, and the ampoule was placed in a thermostat. When the ampoule had acquired the thermostat temperature, the reducing agent was transferred to the iron solution. When the reaction was complete, the ampoule was cooled to −78° and 1 : 1 sulfuric acid solution was sucked in. The hydrocarbon solution was separated from the aqueous layer and thorougly washed with water. The aqueous solution was titrated with 0.1 N $K_2Cr_2O_7$ solution.

Styrene was polymerized in a nitrogen atmosphere in ampoule-dilatometers. It was previously washed free of stabilizer with aqueous caustic alkali, dried and distilled in vacuum. The kinetics of reaction of the components were characterized through the consumption of peroxide which was determined iodometrically.

Analysis of isopropylbenzene hydroperoxide was carried out in an atmosphere of carbon dioxide.

SUMMARY

1. A study was made of the mechanism of action of an oxidation-reduction system comprising isopropylbenzene hydroperoxide (benzoyl peroxide), diethyl dihydroxymaleate (benzoin) and iron naphthenate.

2. Initiation of polymerization in a homogeneous medium under the influence of these systems was demonstrated.

3. It was shown that naphthenates of salts of the -ic form of metals with varying valences in hydrocarbon media greatly speed up the breakdown of isopropylbenzene hydroperoxide, and the possibility of utilizing this reaction for initiation of polymerization was established.

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DETERMINATION OF THE HYDROCARBON COMPOSITION OF GASOLINES OBTAINED FROM PETROLEUMS OF THE TATAR REPUBLIC*

I. GASOLINES OF THE BAVLIN AND ROMASHKINO PETROLEUM DEPOSITS

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S.-Kh. G. Kashaev and B. Le

In the present communication we submit the results of investigation of the nature of the individual hydrocarbons of two gasolines with an end boiling point of 150° from petroleum of the Bavlin and Romashkino deposits of the Tatar Autonomous Republic. Both deposits date from the Devonian period. Bavlin petroleum (well No. 15) was taken in 1952 from the 1st horizon D_1 (Pashisk series); petroleum found at a depth of 1650 meters. The Romashkino oil (well No. 109) was taken in 1953 from the second stratum of the 1st horizon D_1^2 (Pashisk series) at a depth of 1820 meters. The investigation was carried out by the combination method developed in the N. D. Zelinsky Institute of Organic Chemistry of the Academy of Sciences of the USSR and in the P.N. Lebedev Institute of Physics of the Academy of Sciences of the USSR [1]. This procedure had been successfully applied by the authors to the examination of a number of gasolines [2-6] from Soviet petroleums.

TABLE 1

Distribution of the Identified Hydrocarbons by Classes

Class of hydrocarbons	Number of hydrocarbons found in the gasoline	
	Bavlin	Romashkino
Paraffins	29	26
Cyclopentanes	10	11
Cyclohexanes	18	18
Aromatics	6	6
Total	63	61

As a result of our investigations, the gasoline from the Bavlin petroleum was evaluated to the extent of 82.6% (in wt.% of the whole gasoline). The gasoline was found to contain 63 hydrocarbons, of which 62 were quantitatively determined. The gasoline from Romashkino petroleum (in which 61 hydrocarbons were quantitatively determined) was identified to the extent of 80.5%. The distribution of the hydrocarbons by classes is given in Table 1.

The investigated fractions are designated by letters. Gasoline from Bavlin petroleum is known as TsB; that from Romashkino oil as TsR.

EXPERIMENTAL

Isolation of broad fractions (Sh) and their fractional distillation. The investigated petroleums had the characteristics: Bavlin: d_4^{20} 0.8437; paraffin wax content 5.4%; resin (acidic) 26.4%; sulfur 1.22%; Romashkino: d_4^{20} 0.8675; paraffin wax content 4.3%; resin (acidic) 36%; sulfur 1.72%.

* The present account of the individual composition of Tatar gasolines was carried out and generalized by F. A. Urmancheev. During his work he utilized and generalized the data for optical analysis of gasoline fractions obtained by S.—Kh. G. Kashaev, B. Le and M. G. Odintsov. The work was directed by E. A. Robinzon.

TABLE 2

Results of Fractionation of ShB Gasoline

Designation of fraction	Boiling range in °C (760 mm)	Weight in g	Content of fraction in wt.%	
			on ShB	on TsB
K_1B – gases	–	167	5.0	5.7
LB – light fraction	20-45	372	11.2	12.8
AB – main fraction	45-150	2366	71.1	81.5
Residue	above 150	328	9.9	–
Losses	–	95	2.8	–
Total		3328	100.0	

TABLE 3

Results of Fractionation of ShR Gasoline

Designation of fraction	Boiling range in °C (760 mm)	Weight in g	Content of fraction in wt.%	
			on ShR	on TsR
K_1R – gases	–	138	6.8	10.3
LR – light fraction	22-59	156	7.7	11.7
AR – main fraction	59-150	1041	51.0	78.0
Residue	above 150	679	33.3	–
Losses	–	24	1.2	–
Total		2038	100.0	

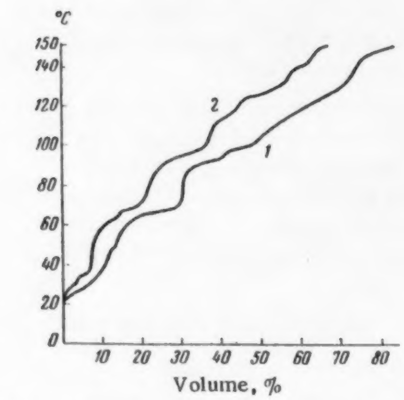

Fig. 1. Distillation curves of fractions: 1) ShB; 2) ShR.

From the petroleum were distilled off fractions (Sh) with an end boiling point of 160° (Bavlin) and 200° (Romashkino). Gaseous hydrocarbons coming off during fractionation were collected in traps cooled to −70°. At the end of the fractionation these were returned to the distillates. The broad fractions were refractionated in a precision column with an efficiency of 35 theoretical plates. The following batches were collected in the fractionation: gaseous portion K_1 (condensate in the gas traps cooled to −70°); volatile portion L (distilling from start of boiling to appearance of benzene in distillate as detected by the formolite reaction); and the main fraction A (from first appearance of benzene up to 150°). Results of fractional distillation are presented in Tables 2 and 3 and plotted in Fig. 1.

The main fractions had the following characteristics: AB – d_4^{20} 0.7191; n_D^{20} 1.4049; aniline point (maximum) 54.5°; sulfur content 0.02 wt.%; AR – d_4^{20} 0.7258; n_D^{20} 1.4081; aniline point (maximum) 50.5°; sulfur 0.03 wt.%.

Fractions K_1, L and A (i.e., all boiling up to 150°) are classified as full gasolines and their amounts were: TsB 2905 g; TsR 1335 g.

Prior to fractionation, the gaseous portion K_1 was freed from C_5 and higher hydrocarbons which were added to the light fraction L. The latter was subjected to debutanization and the butane was added to the light gasoline portion. The lightened gaseous portion (together with the added butane) K was examined in a TsIATIM-51* apparatus; the debutanized light fraction M was subjected to fractional distillation in an efficient column.

* [Central Scientific Research Institute of Aviation Fuels and Oils.]

Examination of Gases K*

The content of individual gaseous hydrocarbons (propane, isobutane and n-butane) in the gaseous fraction was determined by fractional distillation. n-Butane predominated in both of the gasolines.

Investigation of Debutanized Fractions M

Debutanized fractions were distilled in a column with an efficiency of 40 theoretical plates. Fractionation curves were plotted with progressive withdrawal of fractions (Fig. 2). The following fractions were taken off: isopentane (from start of boiling to 32°); n-pentane (32-42°); 42-55° fraction. The 42-55° fractions and residues boiling higher than 55° were examined optically for the purpose of quantitative determination of their content of cyclopentane, 2,2- and 2,3-dimethylbutanes, and 2- and 3-methylpentanes.

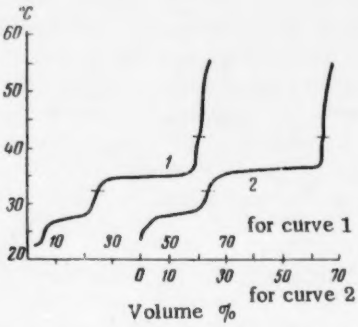

Fig. 2. Distillation curves of fractions: 1) MB; 2) MR.

Investigation of Main Fractions A

1. Separation of aromatic hydrocarbons from their mixture with paraffinic and naphthenic hydrocarbons. Resolution of fractions A into aromatic hydrocarbons B and naphthenic-paraffinic portion C was performed with the help of silica gel and with isolation of intermediate fractions. Complete resolution of the intermediate fraction in the case of Bavlin gasoline required a further chromatographic adsorption using pentane as displacing liquid. In the case of Romashkino gasoline the content of aromatic hydrocarbons in the intermediate fraction was calculated from the refractive index. We made a special experimental check of the accuracy of this method of determination of the aromatic content of gasoline. Separation of the main fraction resulted in isolation of 5.53% (Bavlin) and 5.66% (Romashkino) of a mixture of aromatic hydrocarbons. These are percentages by weight calculated on the whole of the gasoline Ts. The contents of naphthenes and paraffins are respectively 74.2% and 71.4% calculated on the Ts.

2. Examination of aromatic hydrocarbons B. This mixture was fractionated in a column with an efficiency of 40 theoretical plates. At the same time the fractionation curves were plotted and fractions corresponding to benzene, toluene and xylenes were collected. The last two fractions were examined by means of the Raman spectra. All the xylene isomers and ethylbenzene were quantitatively determined in this way; m-xylene predominated.

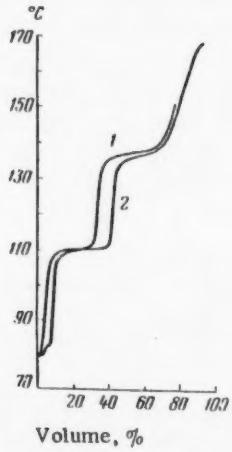

Fig. 3. Distillation curves of fractions: 1) BR; 2) DR.

The distillation curve of aromatic hydrocarbons B from Romashkino gasoline (BR) is plotted in Fig. 3.

3. Examination of the naphthenic-paraffinic fraction C. a) Dehydrogenation of cyclohexane hydrocarbons. The paraffinic-naphthenic fractions C were subjected to catalytic dehydrogenation for transformation of the cyclohexane hydrocarbons into aromatics. This was effected by passing fractions C over iron-containing platinized carbon at 300° at a space velocity of 0.8-0.9 hr^{-1}.

b) Separation of catalyzates into aromatic hydrocarbons and a mixture of paraffins and cyclopentanes. Catalyzates G resulting from dehydrogenation were chromatographed on silica gel to give aromatic hydrocarbons D (originating from dehydrogenation of hexamethylene hydrocarbons) and a paraffin-cyclopentane fraction E. The amount of aromatics separated in this manner was 6.4% on the Ts for Bavlin gasoline and 6.5% for Romashkino gasoline; the mixtures of paraffins and cyclopentanes amounted, respectively, to 64.4 and 61.2% on the Ts.

* The gases were investigated by L. A. Mukhamedova.

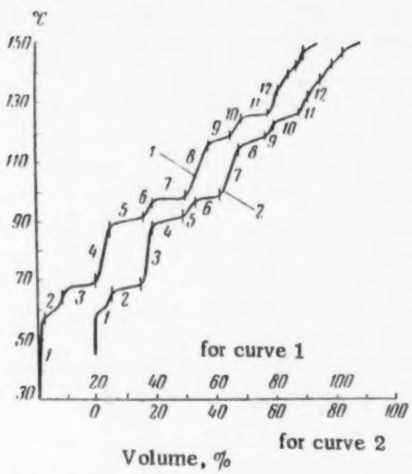

Fig. 4. Distillation curves of fractions: 1) EB; 2) ER.

c) Examination of aromatic hydrocarbons D. The aromatics originating from the hexamethylenes on dehydrogenation were fractionated in a column with an efficiency of 40 theoretical plates. At the same time the fractionation curves were plotted and fractions corresponding to benzene, toluene, xylenes and cumenes were collected; the latter in turn corresponded to the content in the gasoline of cyclohexane, methylcyclohexane, dimethylcyclohexanes and trimethylcyclohexanes, respectively. The individual aromatics were quantitatively determined by optical investigation, and from these results were calculated the amounts of the corresponding cyclohexane hydrocarbons. The distillation curve of the aromatic hydrocarbons D of Romashkino gasoline (DR) is plotted in Fig. 3.

d) Examination of the paraffin-cyclopentane fractions E. These fractions, obtained in chromatographic separation of the aromatic hydrocarbons D, were cut into narrow fractions in a column with an efficiency of 40 theoretical plates. The distillation curves of 100 ml of fraction E from each gasoline were first plotted (Fig. 4). In the case of Bavlin gasoline, 200 ml of fraction E was fractionally distilled and 16 narrow fractions were collected; in the case of Romashkino gasoline, 300 ml was fractionated and 15 narrow fractions collected. Optical methods were employed for quantitative determination in these narrow fractions of normal and isoparaffins and of cyclopentanic and gem-substituted cyclohexanic hydrocarbons.

EXPERIMENTAL RESULTS

The contents of paraffins, cyclopentanes, cyclohexanes and aromatic hydrocarbons in the gasolines were calculated on the basis of the data of the present investigation. All the individual hydrocarbons found in the gasolines were calculated in wt.% of the total gasoline (Ts) and listed in Table 4. This table also contains the quantitative balance of the complete investigation. The data of Table 4 are a basis for establishment of the group composition of the gasolines, especially in connection with the normal and branched-chain paraffins, the cyclopentanes and the cyclohexanes (Table 5).

Tables 4 and 5 show that TsB gasoline contains 61.82% of paraffinic and 16.01% of naphthenic hydrocarbons; the corresponding contents in TsR gasoline are 60.87% and 15.30%. These data show that gasolines from Bavlin and Romashkino petroleums are paraffinic in type and similar in this respect to gasoline from Tuimazin petroleum [4] which contains 66.2% paraffins and 16.5% naphthenes.

If we assume the sum of the paraffinic hydrocarbons to be 100%, then hydrocarbons with normal structure are present in Bavlin gasoline to the extent of 57.6% and in Romashkino gasoline to the extent of 49.9%, and the corresponding values for isohydrocarbons are 42.4% and 50.1%, i. e. , Bavlin gasoline differs from Romashkino in containing a slightly predominating amount of normal paraffins, while the amounts of normal and branched-chain paraffins in Romashkino gasoline are roughly identical.

The branched paraffins in both of the gasolines consist mainly of hydrocarbons with a tertiary carbon atom (99.2-99.8%) with only an insignificant content (less than 1%) of paraffins with a quaternary carbon atom. It should be noted that among the branched-chain prafffins with a tertiary carbon atom are hydrocarbons with two and even three tertiary carbon atoms (2,3,5-trimethylhexane in Romashkino gasoline) which were not detected in Tuimazin gasoline [4].

Gasolines from petroleums of the eastern regions of the USSR, in particular Bavlin gasoline, have octane numbers of the order of 50 [7]. On the basis of data for Bavlin and Romashkino gasolines, the relatively low octane numbers of such gasolines can be explained not only by the high content of paraffins of normal structure but also by the fact that among the isoparaffins there is a predominance of less branched hydrocarbons with low octane numbers, while more highly branched hydrocarbons with high octane numbers (particularly those with quaternary carbon atoms) are nearly absent altogether.

TABLE 4

Individual Hydrocarbons Found in TsB and TsR Gasoline

Name of hydrocarbon	Content in wt.%		Name of hydrocarbon	Content in wt.%	
	on TsB	on TsR		on TsB	on TsR
Paraffinic Hydrocarbons					
Propane	1.06	0.25	2,3-Dimethylpentane	0.35	0.64
n-Butane	5.14	4.97	2,4-Dimethylpentane	0.15	–
Isobutane	0.70	3.16	3-Ethylpentane	0.29	0.37
n-Pentane	5.77	5.37	n-Octane	6.73	5.73
2-Methylbutane	2.91	2.64	2-Methylheptane	2.99	3.54
Neopentane	+	–	3-Methylheptane	1.30	1.34
n-Hexane	6.71	5.41	4-Methylheptane	1.74	1.31
2-Methylpentane	3.69	4.52	2,3-Dimethylhexane	0.91	–
3-Methylpentane	1.78	2.59	2,4-Dimethylhexane	0.68	0.58
2,2-Dimethylbutane	0.07	0.06	n-Nonane	2.21	1.81
2,3-Dimethylbutane	0.38	0.16	2-Methyloctane	0.66	0.72
n-Heptane	7.98	6.79	3-Methyloctane	0.65	0.81
2-Methylhexane	2.43	2.53	4-Methyloctane	0.48	0.73
3-Methylhexane	3.61	3.65	2,3,5-Trimethylhexane	–	0.49
2,2-Dimethylpentane	0.15	–	2,6-Dimethylheptane	0.30	0.70
			Total	61.82	60.87
Cyclopentane Hydrocarbons					
Cyclopentane	0.43	0.28	Ethylcyclopentane	0.68	0.78
Methylcyclopentane	1.83	1.56	1-Cis-2-trans-3-cis-trimethyl-cyclopentane	0.46	0.78
Cis-1,2-dimethylcyclopentane	0.74	0.48	1-Cis-2-trans-4-cis-trimethyl-cyclopentane	0.24	–
Trans-1,2-dimethylcyclopentane	0.99	0.70	n-Propylcyclopentane	0.30	0.31
Cis-1,3-dimethylcyclopentane	0.76	0.44	Isopropylcyclopentane	–	0.07
Trans-1,3-dimethylcyclopentane	0.39	0.52	1-Cis-2-cis-4-trans-trimethyl-cyclopentane	–	0.26
			Total	6.82	6.18
Cyclohexane Hydrocarbons					
Cyclohexane	1.27	1.04	1-Methyl-2-ethylcyclohexane	0.16	0.15
Methylcyclohexane	3.07	2.88	1-Methyl-3-ethylcyclohexane	0.29	0.23
1,1-Dimethylcyclohexane	0.15	0.29	1-Methyl-4-ethylcyclohexane	0.16	0.10
1,2-Dimethylcyclohexane	0.22	0.31	1,1,2-Trimethylcyclohexane	0.09	0.10
1,3-Dimethylcyclohexane	1.12	1.01	1,1,3-Trimethylcyclohexane	1.04	1.31
1,4-Dimethylcyclohexane	0.25	0.32	1,1,4-Trimethylcyclohexane	0.15	0.19
Ethylcyclohexane	0.74	0.83	1,2,3-Trimethylcyclohexane	0.04	0.01
n-Propylcyclohexane	0.10	0.10	1,2,4-Trimethylcyclohexane	0.17	0.10
Isopropylcyclohexane	0.10	0.10	1,3,5-Trimethylcyclohexane	0.07	0.07
			Total	9.19	9.12

(continued)

TABLE 4 (continued)

Name of hydrocarbon	Content in wt.%		Name of hydrocarbon	Content in wt.%	
	on TsB	on TsR		on TsB	on TsR
Aromatic Hydrocarbons					
Benzene	0.67	0.44	% identified	82.55	80.52
Toluene	1.70	1.62	% unidentified	4.91	5.18
Ethylbenzene	0.62	0.65	Residues in flask after fractionation	4.19	6.39
o-Xylene	0.31	0.29	Losses	8.35	7.91
m-Xylene	1.13	1.04			
p-Xylene	0.29	0.31			
Total	4.72	4.35	Total in % on Ts	100.00	100.00

TABLE 5

Group Compositions of TsB and TsR Gasolines

Class of hydrocarbons	Content in %	
	on TsB	on TsR
Normal paraffins	35.60	30.35
Paraffins with tertiary carbon atom	26.00	30.46
Paraffins with quaternary carbon	0.22	0.06
Cyclopentanes	6.82	6.18
Cyclohexanes	9.19	9.12
Aromatics	4.72	4.35

The following picture emerges of the group composition of the hydrocarbons with identical molecular weight. Of the C_5 and C_6 hydrocarbons, the gasolines contain all of the possible isomers with the exception of neopentane in Romashkino gasoline. All of the C_7 isomers are detected with the exception of 2,2,3-trimethylbutane and 3,3-dimethylpentane, i. e., hydrocarbons with a quaternary carbon atom. The third isomer with a quaternary carbon atom(2,2-dimethylpentane) is found only in Bavlin gasoline and only to the extent of 0.15% on the TsB. The C_8 hydrocarbons found in the gasolines are n-octane, all of the three methylheptanes and 2,3- and 2,4-dimethylhexanes (the 2,3-isomer is present only in Bavlin gasoline). The content of more highly branched isooctanes in the gasolines was not established. C_9 hydrocarbons are represented by n-nonane, all of the three methyloctanes, 2,6-dimethylheptane and 2,3,5-trimethylhexane (in Romashkino gasoline).

Cyclopentane hydrocarbons are present in TsB gasoline to the extent of 6.8%, and in TsR to the extent of 6.2%. 0.43% of cyclopentane was found in TsB, and 0.28% in Romashkino (0.37% in Tuimazin). Methylcyclopentane predominates among the cyclopentane hydrocarbons with one side chain. Methylcyclopentane hydrocarbons with two side chains are represented by all of the dimethylcyclopentanes with exception of 1,1-dimethylcyclopentane, while those with three side chains are represented by 1-cis-2-trans-3-cis-trimethylcyclopentane, 1-cis-2-trans-4-cis-trimethylcyclopentane (in TsB) and by 1-cis-2-cis-4-trans-trimethylcyclopentane (in TsR); in both of the gasolines the member of this group that predominates is 1-cis-2-trans-3-cis-trimethylcyclopentane.

The content of cyclohexane hydrocarbons is 9.2% in TsB and 9.1% in TsR. In comparison with the other cyclohexane hydrocarbons, the most plentiful is methylcyclohexane (3.07% in TsB and 2.88% in TsR). Among the cyclohexanes with two methyl groups, 1,3-dimethylcyclohexane predominates. Among the methylethylcyclohexanes, the most plentiful is the 1,3-isomer. The predominating representative of the trimethylcyclohexanes is 1,1,3-trimethylcyclohexane which contains a quaternary carbon atom.

The content of aromatics is 4.7% in TsB and 4.4% in TsR. As in the case of the cyclohexane hydrocarbons, there is a predominance of representatives with one side chain and with two side chains in the meta-position.

The chemical side of the investigation of gasolines was undertaken in the petroleum chemical laboratory of the A. E. Arbuzov Institute of Chemistry of the Kazan Branch of the Academy of Sciences, USSR; the optical investigation was carried out by the spectral laboratory of the Institute of Technical Physics of the Kazan Branch of the Academy of Sciences, USSR.* Assistant E. P. Trutneva took part in the optical examination.

* The results of the optical analysis of the gasolines were made much more precise with the help of Kh. E. Sterin, a member of the Spectroscopic Committee of the Academy of Sciences, USSR, to whom we convey our thanks.

SUMMARY

1. The combination method of examination of the individual hydrocarbon composition of straight-run gasolines was applied to the analysis of two samples of gasoline with an end boiling point of 150° from the Bavlin and Romashkino oil deposits of the Tatar Republic located in the first horizon of the Devonian (Pashisk series).

2. It was shown that the chemical characters of the investigated gasolines of petroleums of the same age from one and the same level are identical, apart from slight fluctuations in the content of paraffinic hydrocarbons of normal and iso structure.

3. Of the paraffinic normal hydrocarbons, all of the possible hydrocarbons from propane through nonane were found in the investigated gasolines. Of the naphthenic hydrocarbons, we found cyclopentane, cyclohexane and some of their immediate homologs with predominance of methylcyclopentane and methylcyclohexane. The ratio between the quantities of cyclopentane and cyclohexane hydrocarbons is 0.74 for Bavlin gasoline and 0.68 for Romashkino gasoline. Aromatic hydrocarbons were represented by benzene, toluene, ethylbenzene and o-, m- and p-xylenes. In both of the gasolines the amounts of individual aromatics increased in the order: p- and o-xylenes, ethylbenzene and benzene, m-xylene, toluene.

4. The low octane numbers of gasolines from petroleums of the eastern regions of the USSR are due to the high content of normal paraffins and also (apparently) to the remarkably small proportion in these isoparaffins of highly branched hydrocarbons with high octane numbers.

5. The method of examination of gasolines developed in the Institute of Organic Chemistry and the Institute of Physics of the Academy of Sciences, USSR was successfully employed for investigation of gasolines from the sulfur-containing petroleums of the Tatar Republic (the crudes contained 1.2-1.7% sulfur and the gasolines 0.02-0.03% sulfur).

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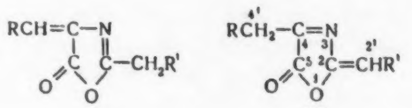
Branch of the Academy of Sciences, USSR

* Original Russian pagination. See C. B. translation.

STRUCTURE AND PROPERTIES OF OXAZOLONES

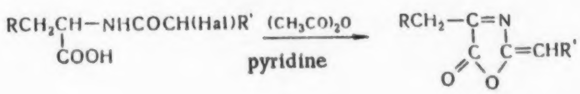
O. V. Kildisheva, M. G. Linkova and I. L. Knunyants

Although a great deal of experimental data has become available in recent years in the field of the chemistry of oxazolones, the structure of these compounds has not been fully elucidated. In this case (just as in many other cases) it was natural that attention should be fixed on the possibility of tautomerism between the real (I) and the pseudo (II) form of oxazolones:



(I) (II)

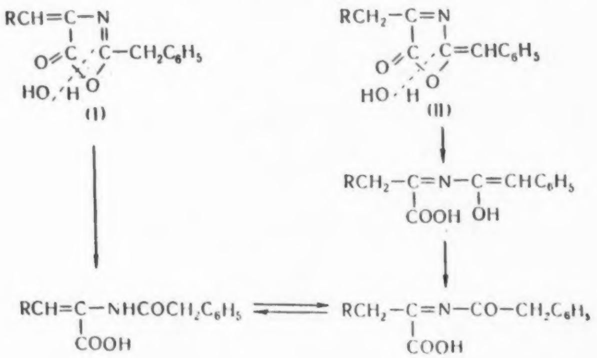
From this standpoint, not one of the methods of preparation of these substances, although leading from the purely structural standpoint to one and the same forms, could be adduced as proof of the structure of these substances. Thus, one of the methods of obtaining oxazolones from α-haloacyl derivatives of α-amino acids [1] (Bergmann's method) inevitably leads to the conclusion that unsaturated oxazolones possess the pseudostructure (II).



(II)

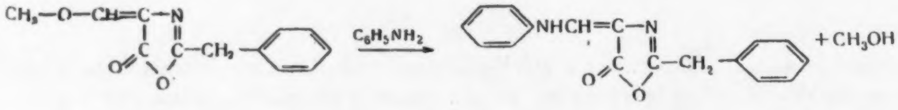
By this method were obtained oxazolones bearing alkthio, alkoxy, alkyl or aryl groups as substitutents in position 4 of the oxazolone ring, while bearing alkaryl but not aryl groups in position 2.

None of the reactions of oxazolones associated with preliminary opening of the oxazolone ring can be regarded as evidence in favor of one structure or the other, because the products of cleavage of the true and pseudo oxazolones will be identical, again because of the possibility of their tautomerism or their passage from one form into the other.

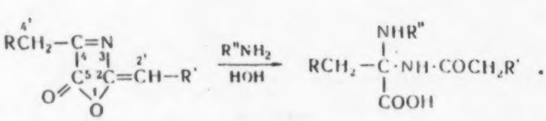


Close acquaintance, however, with the chemical properties of the majority of oxazolones prepared by Bergmann's method inevitably leads to the conclusion that these compounds are true oxazolones with structure (I).

The principal criterion for interpretation of the structure in this case is the susceptibility of these oxazolones, bearing alkoxy, alkthio or alkamino groups in position 4, to replacement of these groups by other residues of nucleophilic reactants (methoxy replaced by alkamino or alkthio; alkthio replaced by alkamino, etc. [2]):

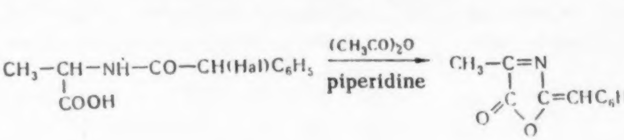


Reactions of this type are clearly impossible with the pseudo structure. Reaction of nucleophilic reactants with pseudooxazolones ought to lead to products of entirely different structure, which have never been detected in any of the cases cited above. In the event of presence of an arylidene grouping in position 4, the criterion is similarly the susceptibility of addition of nucleophilic reactants, such reactions being usually accompanied by cleavage of the oxazolone ring. Consequently, oxazolones obtained by the Bergmann method and bearing alkoxy or analogous structures (orientants of the first order) in position 4 are true oxazolones with structure (I). Experiments lead moreover to the conclusion that the pseudo structure is formed in the Bergmann reaction with α-haloacylamino acids bearing in the β-position groupings that ensure maximum conjugation of the pseudo structure of the oxazolones formed. In this case unequivocal proof of the pseudooxazolone structure is afforded, as our experiments have shown, by a series of 4,2'-addition reactions (1—4-addition) with formation of α-acylaminocarboxylic acids bearing the residue of the added reactant in α-position. This would not have been the case if the true oxazolone structure were involved.

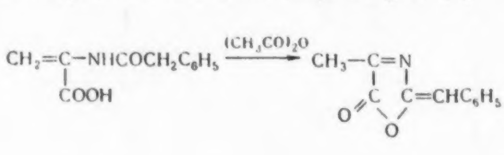


(II)

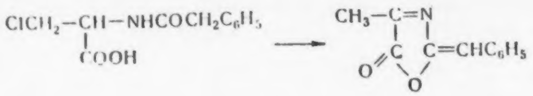
Pseudooxazolones are also formed in a series of other methods of preparation of oxazolones in all cases when the substituents in positions 2 and 4 ensure maximum conjugation in the pseudooxazolone structure. Thus, 4-methyl-2-benzylidene-pseudooxazolone, whose structure was confirmed by spectra and by synthesis of the ester of α-phenylamino-α-phenacetylaminopropionic acid [2], was obtained from α-(N-α'-haloacetophenyl)-aminopropionic acid by the action of acetic anhydride and piperidine:



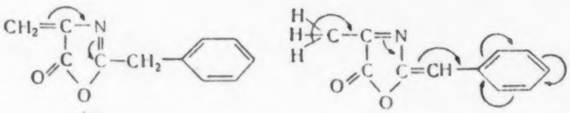
Treatment of α-phenacetylaminoacrylic acid with acetic anhydride gives [3]



The same result is obtained by treatment of β-chloro-α-phenacetylaminopropionic acid with acetic anhydride, thionyl chloride, pyrophosphite, etc. [4].

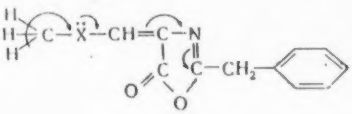


All these methods lead to the pseudooxazolone (II) due to the susceptibility of the methyl group to hyperconjugation:



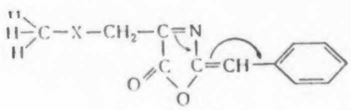
(I) (II)

It is clear that this pseudooxazolone system is more highly conjugated than the true oxazolone system (I) whose conjugation is interrupted by the methyl group between the oxazolone and benzene rings. As already mentioned above, if the structure of the original product includes a substituent in position 4 of the oxazolone ring that creates the possibility of greater conjugation in the true structure than in the pseudo structure, then a true oxazolone is formed. This can be demonstrated by the following examples:



, where X = O, NH, S, etc.

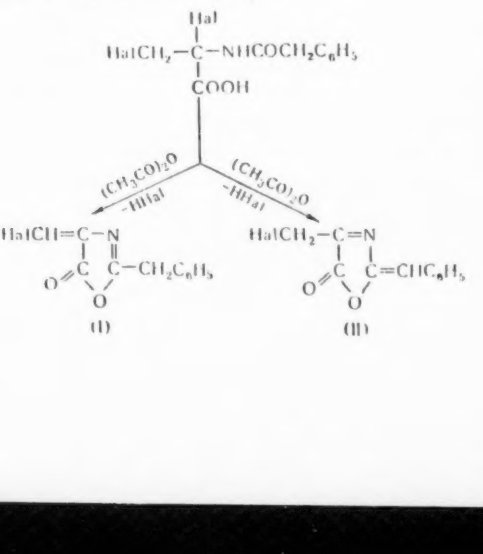
(I)



(II)

It is evident that the conjugation of structure (I) is greater than that of structure (II) due to the weak conjugation with the terminal benzene ring. In this manner we establish clearly the distinction between the true and the pseudo structure of oxazolone.

In the present investigation our objective was the study of the structure of oxazolones obtained by dehydration of α,β-dihalo-α-phenacetylaminopropionic acids [5].



(I) (II)

Measurement of the absorption spectra showed that these compounds are pseudo oxazolones (II). Thus, the ultraviolet absorption spectrum of 2-benzylidene-4-bromomethyloxazolone has two strong bonds characteristic of pseudooxazolone structures (Fig. 1).

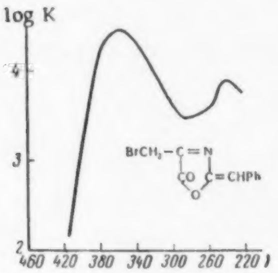
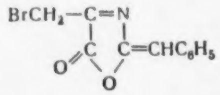
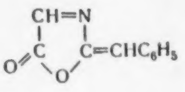


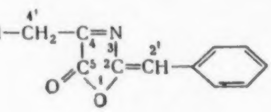
Fig. 1.

	1st band	2nd band
	3600	2400
	3580	2360 [6]

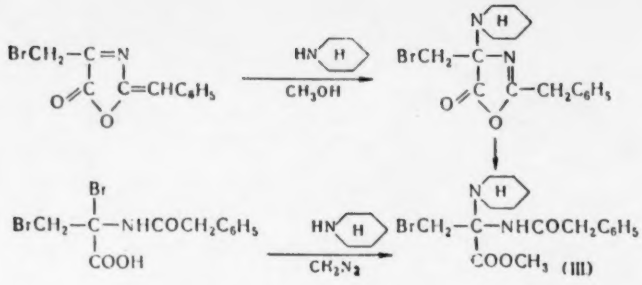
Superficial consideration of the pseudo structure of these oxazolones, which bear a halomethyl group in position 4 of the oxazolone ring, might lead to the opposite view of the structure of oxazolones that differ from those studied by the fact that the halogen atom is replaced by the alkthio or alkoxy groups. Such compounds were previously (see above) assigned the structure of true oxazolones.

It is quite obvious that alkthio or alkoxy groups lead to undoubtedly more conjugated systems than are formed with the halogen atom, due to the hyperconjugation of the methyl group with the free electron pairs of the atom of sulfur and oxygen and to the subsequent conjugation of these pairs with the double bonds of the oxazolone ring. The distinction between the susceptibility to conjugation of the hydroxy, alkoxy, alkthio and alkamino groupings on the one hand and that of the halogen atom on the other hand also follows from the known facts of the greater stability of the benzene ring of chlorobenzene in substitution reactions in comparison with the remaining monosubstituted derivatives of benzene bearing other first-order substituents. However, the pseudooxazolone structure of these oxazolones was also confirmed by reactions with nucleophilic reactants.

As was pointed out above, pseudooxazolones add on nucleophilic reactants in the 4,2'-position (1—4-addition), but in regard to the reactivity of 2-benzylidene-4-halomethyl-pseudooxazolones-5 towards nucleophilic reactants these oxazolones must in the general case contain some vacant positions for initial attack by the residue of the nucleophile, namely a strongly positively polarized (due to conjugation) ring carbon atom in position 4, two positively polarized carbonyl carbons in positions 2 and 5:

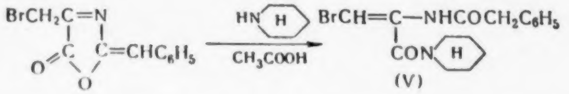


The attack of the carbon atom of the halomethyl group ought theoretically to be weakened by the strong positive polarization of the 4th carbon atom linked with it. The problem of the degree of electrophilicity of the atoms 4, 2 and 5, and in turn of the order of attack on them by nucleophiles could only be solved by experiments. Investigation of the reaction of 2-benzylidene-4-bromomethyl-pseudooxazolone-5 with piperidine showed that piperidine in methanol solution attacks position 4 of the oxazolone ring with formation of a saturated oxazolone which immediately reacts with the alcohol with formation in quantitative yield of the methyl ester of α-piperidino-α-phenacetylamino-β-halopropionic acid (III) with m. p. 106°.



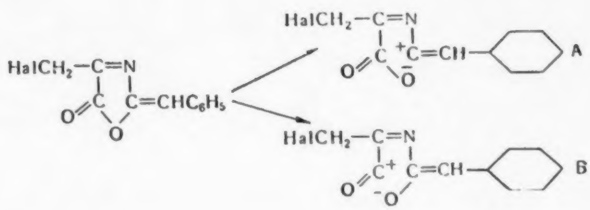
(III)

The structure of the ester (III) was confirmed by synthesis of the same ester from α, β-dibromo- α-phenacetylaminopropionic acid. As was shown earlier, in α, β-dihalo- α-acylaminocarboxylic acids the halogen in the α-position is considerably more active than that in the β-position [7], so that the action of piperidine on an ethereal solution of α, β-dibromo- α-phenacetylaminopropionic acid gave α-piperidino-α-phenacetylamino-β-bromopropionic acid (IV) in the form of a salt with piperidine; with diazomethane the latter gave a methyl ester identical with the methyl ester of α-piperidino-α-phenacetylamino-β-bromopropionic acid (III). Moreover, the same oxazolone reacted with piperidine in an ethereal solution of acetic acid with formation of the piperidine of β-bromo-α-phenacetylaminoacrylic acid (V), m. p. 105-106°. The attack in this case was first directed at the carbon atom in the 5 position of oxazolone:

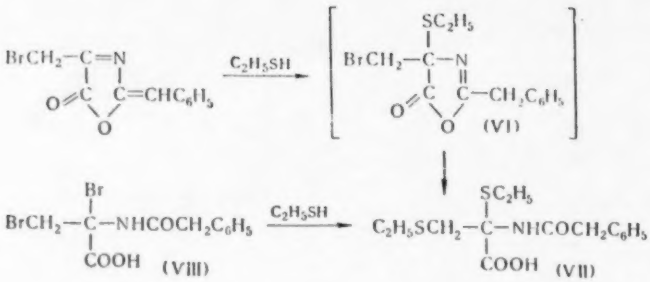


(V)

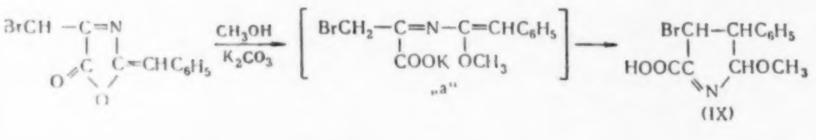
In this case it is natural that the reduction in the nucleophilicity of piperidine due to salt formation should render the piperidine incapable of attack at the carbon atom in position 4, addition to which may be regarded as fully comparable with Sn 2-nucleophilic substitution. However, the attack by piperidine acetate on carbon atom 5 in this case is decisive evidence that the very much slower cleavage of the oxazolone ring by weak nucleophiles proceeds by the Sn1 mechanism; this mechanism is facilitated by the ionizing medium of acetic acid:



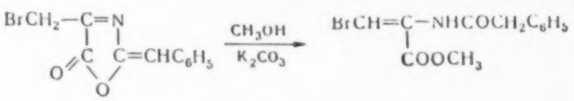
In the light of these considerations, very great interest was attached to investigation of reactions of pseudooxazolones with other nucleophilic reactants such as, for example, mercaptans and alcohols. As had been expected, the action of excess of ethylmercaptan (a strong nucleophile) in presence of potassium carbonate on 2-benzylidene-4-bromomethyl-pseudooxazolone-5 led to addition of the mercaptan, just like the piperidine mentioned above, in position 4,2' (1—4-addition). Further reaction of the intermediate compound (VI) with ethylmercaptan led to its transformation into α, β-diethylthio- α-phenacetylaminopropionic acid (VII), m. p. 128-130°. This was identical with the acid obtained by interaction of ethylmercaptan with α, β-dibromo- α-phenacetylaminopropionic acid (VIII) [8].



Unlike the reactions with mercaptans and amines, the reaction with alcohols (which are weaker nucleophiles and therefore incapable of reacting with the carbon in position 4 as was to be expected in the light of the foregoing discussion) is accompanied by cleavage of the oxazolone ring at the carbon in position 2 (and not in position 5). For example, the action of methanol in presence of potassium carbonate on 2-benzylidene-4-bromomethyl-pseudooxazolone-5 leads to separation of the potassium salt of the acid (IX), due to which a molar proportion of potassium carbonate is consumed. Acidification gave the free acid (IX) with m. p. 138-140° (with decomposition):

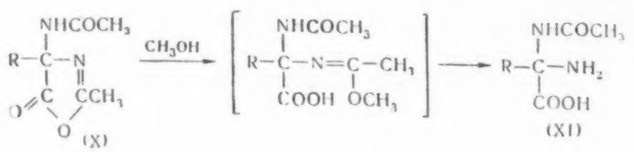


The more normal reaction with an alcohol, however, would involve attack at carbon atom 5, as usually occurs in the case of the majority of oxazolones with formation of the corresponding esters:

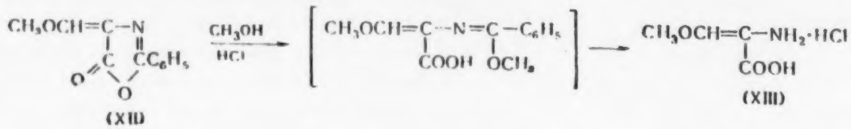


Attack by an alcohol of the carbon in the 2 and not in the 5 position is probably due to ionization of the oxazolone taking place preferentially in position A (p. 741), and the nature of the structure of the intermediately formed acid "a" makes it susceptible to cyclization with formation of 2-methoxy-3-phenyl-4-bromopyrroline-5-carboxylic acid (IX).

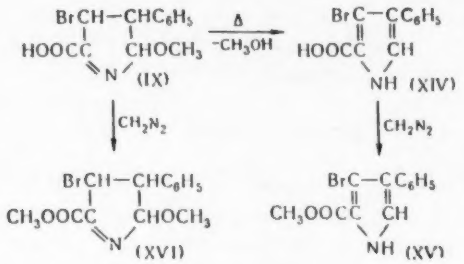
It may be mentioned that similar cases of cleavage of the oxazolone ring have been observed in the past. Thus, 2-methyl-4-acetylamino-4-methyloxazolone [9] or 2-methyl-4-acetylamino-4-chloromethyloxazolone (X) reacts with facility with an alcohol in the absence of moisture with formation of the corresponding α-amino-α-acetylaminopropionic acids (XI). The following is the most probable mechanism of this reaction:



Schulz [10] reacted absolute alcohol, saturated with HCl, with 2-phenyl-4-methoxymethyleneoxazolone-5 (XII) and obtained β-methoxy- α-aminoacrylic acid (XIII):

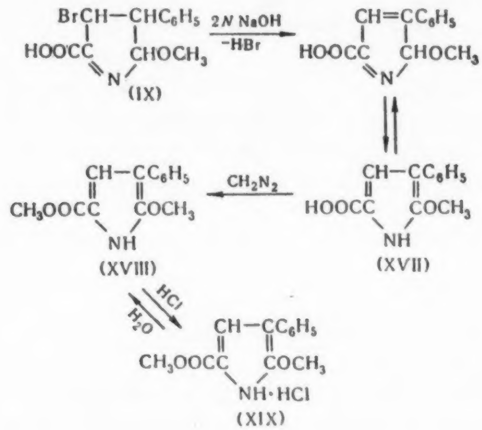


Further investigation of acid (IX) showed that on heating it readily loses a molecule of alcohol and forms 3-phenyl-4-bromopyrrole-5-carboxylic acid (XIV), m. p. 168-170°; with diazomethane the latter reacts to give the methyl ester (XV) with m. p. 133-134°. Heating of an alcoholic solution of ester (XV) with a hydrochloric acid solution of p-dimethylaminobenzaldehyde led to the pink color characteristic of pyrrole. With diazomethane, acid (IX) gave the methyl ester of 2-methoxy-3-phenyl-4-bromopyrroline-5-carboxylic acid (XVI), m. p. 151-152°. The latter proved to be more stable than the original acid and did not split off alcohol when heated.



Prolonged action of 2N NaOH at room temperature on acid (IX) results in loss of HBr with formation of 2-methoxy-3-phenylpyrrole-5-carboxylic acid (XVII) with m. p. 295°. For understandable reasons (the absence of a hydrogen atom in position 3 of the pyrrole ring), alcohol is not split off when acid (XVII) is heated, just as HBr is not split off when 2N NaOH acts on compound (XIV).

Action of diazomethane on (XVII) readily gave the methyl ester (XVIII) with m. p. 159-160°. When treated with dry HCl the ester forms the hydrochloride



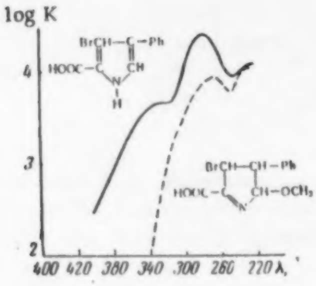


Fig. 2.

of the methyl ester of 2-methoxy-3-phenylpyrrole-5-carboxylic acid (XIX), m. p. 125°; treatment of the latter with water again converts it into the original ester (XVIII). Treatment of acid (XIV) with one mole of bromine in chloroform solution leads to replacement of carbonyl group by bromine with formation of 3-phenyl-4,5-dibromopyrrole (XX), m. p. 144-146°.

The structure of compounds (IX) and (XIV) was confirmed by measurement of the absorption spectra. Examination of the infrared spectra showed that compound (IX) contains a C=O band (1673 cm^{-1}) similar to the C=O band in the carboxyl group; it also contains a C=N band (1643 cm^{-1}) conjugated with the carboxyl group; a band corresponding to C—O—C was also detected in the 1094 cm^{-1} region. The spectrum of (XIV) likewise contains a C=O band but not a C—O—C band. The ultraviolet absorption spectrum of compound (XIV) reveals the appearance of a new double bond in conjugation with the other double bonds (Fig. 2). Consequently we have confirmation, both from the absorption spectra and from the chemical reactions, that compound (IX), obtained by reaction of 2-benzylidene-4-bromomethyl-pseudooxazolone-5 with methanol, is a pyrrole derivative.

EXPERIMENTAL

Methyl Ester of α-Piperidino-α-phenacetylamino- β-bromopropionic Acid (III)

1. To a suspension of 1.3 g (0.005 mole) of 2-benzylidene-4-bromomethyl-pseudooxazolone in 6 ml absolute methanol was added 0.6 ml piperidine in 6 ml methanol. Slight heat was developed and the whole went into solution. A precipitate appeared after 2-3 minutes and was filtered and washed with methanol. 1.5g (80%) of the methyl ester of α-piperidino-α-phenacetylamino- β-propionic acid was obtained; m. p. 106° (with decomposition). The ester is soluble in 2N HCl; on neutralization it comes down unchanged.

Found %: C 53.13; H 6.1; Br 20.42; N 7.43. $C_{17}H_{33}O_3N_2Br$. Calculated %: C 53.26; H 6.0; Br 20.88; N 7.31.

0.05 g of (III) was mixed with 1 ml absolute methanol, 1 ml of 2N NaOH was added and the mixture was left overnight at room temperature. The alcohol was then evaporated off in vacuum and the residue was dissolved in 2 ml water and acidified with 2N HCl. Addition of a solution of 2,4-dinitrophenylhydrazine gave 0.06 g of the dinitrophenylhydrazone of phenacetyloxypyroracemic acid. A mixture with an authentic specimen melted without depression.

2. To a solution of 1.8 g (0.005 mole) of α, β-dibromo- α-phenacetylaminopropionic acid in 30 ml absolute ether was gradually added 0.93 ml (0.01 mole) of piperidine in 5 ml absolute ether. The precipitate was filtered off, washed with absolute ether, suspended in 30 ml absolute ether and treated with an ethereal solution of diazomethane. The insoluble solid was filtered off and the ether was evaporated off. The methyl ester of α-piperidino-α-phenacetylamino- β-propionic acid was thus obtained with m. p. 102-103° (from ether). A mixed specimen with the substance prepared from the pseudooxazolone did not show a depression of melting point.

Piperidideof β-Bromo- α-phenacetylaminoacrylic Acid (V)

To a solution of 0.26 g (0.001 mole) of 2-benzylidene-4-pseudooxazolone-5 in 5 ml absolute ether was added 0.18 ml (0.003 mole) of glacial acetic acid followed by 0.17 ml (0.002 mole) piperidine in 2 ml of absolute ether. In 30-40 minutes (after disappearance of the qualitative reaction for pseudooxazolone), the ethereal solution was washed with 2N HCl and then with water, dried and evaporated to drive off the ether. There was obtained 0.15 g of the piperidide of β-bromo- α-phenacetylaminoacrylic acid with m. p. 105-106° (from ether).

Found %: C 54.22; H 5.5; Br 22.76; N 8.00. $C_{16}H_{19}O_2BrN_2$. Calculated %: C 54.70; H 5.41; Br 22.79; N 7.97.

α, β-Diethylthio- α-phenacetylaminopropionic Acid (VII)

0.532 g (0.002 mole) of 2-benzylidene-4-bromomethyl-pseudooxazolone-5 was mixed with 0.2 g of well-pulverized anhydrous potassium carbonate; 5 ml of ethylmercaptan was then added and the mixture left at room temperature until the reaction for pseudooxazolone was negative. The excess of ethylmercaptan was driven off in vacuum and the residue was treated with water (10 ml); the insoluble oil was extracted with ether and the aqueous layer was acidified with 2N H_2SO_4. There was thus obtained 0.3 g of α, β-diethylmercapto- α-phenacetylaminopropionic acid with m. p. 127-128° (from ether and then water). A mixed specimen with the acid prepared from α, β-dibromo- α-phenacetylaminopropionic acid melted without depression.

2-Methoxy-3-phenyl-4-bromopyrroline-5-carboxylic Acid (IX)

1.3 g (0.005 mole) of 2-benzylidene-4-bromomethyl-pseudooxazolone-5 was mixed in 25 ml absolute methanol with 0.35 g (0.005 mole) of finely pulverized potassium carbonate. Very rapid stirring (for 30-40 minutes) led to complete solution. The alcohol was evaporated off at 20°, the dry residue was dissolved in 20 ml water and the suspension was filtered off and acidified with 2N H_2SO_4 until acidic to congo. There was obtained 2-methoxy-3-phenyl-4-bromopyrroline-5-carboxylic acid with m. p. 138-140° (after precipitation from bicarbonate). Yield 52%. The melting point was measured by inserting the capillary into an apparatus previously heated to 135°. The compound melted at 138-140°, then solidified and melted again (with decomposition) at 158-160°; the last melting point corresponded to the compound which had lost a molecule of alcohol.

Found %: C 48.21; H 4.16; Br 26.00; N 4.37. $C_{12}H_{12}O_3BrN$. Calculated %: C 48.32; H 4.02; Br 26.84; N 4.7.

3-Phenyl-4-bromopyrrole-5-carboxylic Acid (XIV)

2-Methoxy-3-phenyl-4-bromopyrroline-5-carboxylic acid loses a molecule of alcohol when heated for 5-7 minutes in water or HCl (specific gravity 1.19), and forms 3-phenyl-4-bromopyrrole-5-carboxylic acid, m. p. 168-170° (from ethyl acetate).

Found %: C 49.75; H 3.04; Br 29.11; N 4.97. $C_{11}H_8O_2NBr$. Calculated %: C 49.62; H 3.00; Br 30.0; N 5.26.

Methyl Ester of 3-Phenyl-4-bromopyrrole-5-carboxylic Acid (XV)

0.2 g of 3-phenyl-4-bromopyrrole-5-carboxylic acid was treated with an ethereal solution of diazomethane to form the methyl ester of 3-phenyl-4-bromopyrrole-5-carboxylic acid, m. p. 133-134° (from ether).

Found %: C 51.10; H 3.74; Br 27.13; N 4.82. $C_{12}H_{10}O_2NBr$. Calculated %: C 51.4; H 3.57; Br 28.05; N 5.00.

Methyl Ester of 2-Methoxy-3-phenyl-4-bromopyrroline-5-carboxylic Acid (XVI)

0.2 g of 2-methoxy-3-phenyl-4-bromopyrroline-5-carboxylic acid was suspended in ether (2 ml) and treated with an ethereal solution of diazomethane to give 0.18 g of the methyl ester of 2-methoxy-3-phenyl-4-bromopyrroline-5-carboxylic acid, m. p. 151-152° (from ether).

Found %: C 49.75; H 4.46; N 4.47; Br 26.00. $C_{13}H_{14}O_3NBr$. Calculated %: C 50.00; H 4.49; N 4.49; Br 25.6.

2-Methoxy-3-phenylpyrrole-5-carboxylic Acid (XVII)

0.6 g (0.002 mole) of 2-methoxy-3-phenyl-4-bromopyrroline-5-carboxylic acid was kept in 2 ml of 2N NaOH at room temperature for 72 hours and then acidified with 2N H_2SO_4. 2-Methoxy-3-phenylpyrrole-5-carboxylic acid was thus obtained with m. p. 295° (precipitated from $NaHCO_3$ solution); yield 74%.

Found %: C 66.38; H 5.10. $C_{12}H_{11}O_3N$. Calculated %: C 66.3; H 5.06.

Methyl Ester of 2-Methoxy-3-phenylpyrrole-5-carboxylic Acid (XVIII)

0.217 g (0.001 mole) of 2-methoxy-3-phenylpyrrole-5-carboxylic acid was suspended in 1 ml methanol and an ethereal solution of diazomethane was added. The methyl ester of 2-methoxy-3-phenylpyrrole-5-carboxylic acid was thus obtained; m. p. 159-160° (from ether).

Found %: C 67.40; H 5.73; N 5.78. $C_{13}H_{13}O_3N$. Calculated %: C 67.53; H 5.62; N 6.06.

Ester (XVIII) forms a hydrochloride on treatment with alcoholic HCl; m. p. 125° (with decomposition); the hydrochloride readily hydrolyzes in water to form the original ester (XVIII).

3-Phenyl-4,5-dibromopyrrole (XX)

0.2 g of 3-phenyl-4-bromopyrrole-5-carboxylic acid was suspended in 5 ml of chloroform and treated with 10% solution of bromine in chloroform (1 mole). The suspension was filtered off and the filtrate evaporated in vacuum. The residue was triturated with saturated sodium bicarbonate solution; the precipitate was filtered off, dried, and twice recrystallized from ether. 3-Phenyl-4,5-dibromopyrrole was obtained with m. p. 144-146°.

Found %: C 40.41; H 2.47; Br 54.5. $C_{10}H_7Br_2N$. Calculated %: C 40.00; H 2.32; Br 53.2.

We have to thank Yu. N. Sheinker for carrying out the spectral measurements.

SUMMARY

1. On the basis of consideration of the chemical and physical properties of unsaturated oxazolones, it is shown that the formation of true or pseudooxazolones depends upon the substituents of the oxazolone ring in positions 2 and 4, a structure with the most highly conjugated system being formed regardless of the method of formation.

2. 2-Benzylidene-4-halodimethyloxazolones, obtained by dehydration of α,β-dihalo-α-phenacetylaminopropionic acids, are pseudooxazolones.

3. It is shown that 2-benzylidene-4-halomethyl-pseudooxazolones react with nucleophilic agents in different ways depending upon the degree of their nucleophilicity. Strong nucleophiles add on to 2-benzylidene-4-halomethyl-pseudooxazolones in the 4,2'-position (1—4-addition), and the ring of the resultant saturated oxazolone at once opens with formation of α-substituted derivatives of β-halo-α-phenacetylaminopropionic acids. Weak nucleophiles, incapable of nucleophilic attack at the carbon atom in position 4 of the oxazolone ring, bring about cleavage of the ring at position 2. This process leads ultimately to formation of pyrrole derivatives.

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HETEROCHAIN POLYESTERS

1. POLYESTERS OF ISOMERIC PHTHALIC ESTERS

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Preceding communications [1-7] on polyesters of various polymethylene glycols and dicarboxylic acids of the general formula $HOOC(CH_2)_nCOOH$, where n = 0 to 8, dealt with the influence of the structure of the starting glycols and acids on the physical properties of the polyesters obtained therefrom. It was of interest to supplement the work by a study of various polyesters of aromatic dicarboxylic acids. The existing literature [8, 9] reveals that polyesters of aromatic and aliphatic dicarboxylic acids differ considerably from one another in physical properties. Thus, for example, polyethylene terephthalate melts at 265° [9], whereas the majority of polyesters of aliphatic dicarboxylic acids melt below 100°. Edgar and Hill [10] attribute the high melting point of polyethylene terephthalate to the influence of such factors as the great rigidity of the chain due to the p-phenylene groups, the increased polarity of the carbonyl groups due to their conjugation with the double bonds of the benzene ring, which leads to strong interaction of the ester groups, and the formation of hydrogen bonds between the ester groups and the hydrogen atoms of the benzene ring. Batzer and Fritz [11, 12] consider the main reason to be the high degree of symmetry of the macromolecules due to the great symmetry of terephthalic acid itself.

At the present time it is still impossible, in our opinion, to say definitely which of these causes is the decisive one, since the available data for aromatic polyesters are very fragmentary. The present paper is devoted to an investigation of polyesters of the isomeric phthalic acids (phthalic, isophthalic, terephthalic) with such glycols as ethylene glycol, propylene glycol, 1,3-butanediol, pentamethylene glycol, hexamethylene glycol, decamethylene glycol, eicosamethylene glycol, diethylene glycol and triethylene glycol. Some of these polyesters have already been described in the literature [8, 9, 13-28].

EXPERIMENTAL

Polyesters were prepared by the method of transesterification from the dimethyl esters of the corresponding acids and glycols in presence of lead oxide as catalyst. The reaction was usually carried out with a 1 : 2 ratio of dimethyl ester to glycol, and only in the case of the polyesters of eicosamethylene glycol was the ratio altered to 2:1. The proportion of lead oxide was 0.25% on the weight of the component taken in the smaller quantity. The procedure for polycondensation has already been described by us in detail [2, 4].

The prepared polyesters were examined for specific viscosity of their 0.5% solutions in cresol or benzene, for solubility in benzene and alcohol, for boiling point, and for the temperature of transition into a viscous liquid and into the liquid state. The melting points of the solids were determined in capillaries, and those of the liquid and rubbery substances in test tubes after freezing in a mixture of dry ice and acetone. The temperatures of transition into the viscous liquid and liquid states were determined in the Heppler consistometer with a load on the specimen of 1 kg per 1 cm^2 surface.

The temperature of transition into the viscous liquid state was recorded at the instant when the specimen began to be deformed. The temperature of transition into the liquid state was recorded when the rate of deformation of the specimen was 0.2 mm per 1°. Solubilities in benzene and alcohol were determined by the procedure previously described [6]. Results obtained are presented in Tables 1-3.

TABLE 1

Properites of Polyesters of Terephthalic Acid and Various Glycols

Name of glycol	Specific viscosity of 0.5% solution of polyester in cresol	Temperature in °C			Solubility of polyester in g/liter	
		of melting	of transition to viscofluid state	of fluidity	in benzene	in alcohol
Ethylene glycol	0.37	256	–	–	insoluble	insoluble
Trimethylene glycol	0.20	217-218	–	–	–	–
1,4-Butanediol	0.37	222-223	–	–	0.1	insoluble
1,5-Pentanediol	0.27	134-140	–	–	2.2	0.8
1,6-Hexanediol	0.45	148-154	–	–	0.9	insoluble
1,10-Decanediol	0.54	123-127	109	–	0.6	"
1,20-Eicosanediol	0.20	108-113	113	–	1.9	0.3
1,2-Propanediol	0.13	106-111	84	97	> 50	1.6
1,3-Butanediol	0.11	82-87	28.5	37	> 50	3.6
Diethylene glycol	0.44	65-70	34	51	15.1	1.2
Triethylene glycol	0.48	60-65	4	17	11.3	1.1

TABLE 2

Properties of Polyesters of Isophthalic Acid and Various Glycols

Name of glycol	Specific viscosity of 0.5% solution of polyester in crestol	Temperature in °C			Solubility of polyester in g/liter	
		of melting	of transition to viscofluid state	of fluidity	in benzene	in alcohol
Ethylene glycol	0.24	103-108	73	89	2.25	0.2
Trimethylene glycol	0.20	92-96	43	74	–	–
1,4-Butanediol	0.27	88-94	47	60	0.96	0.4
1,5-Pentanediol	0.25	76-82	28	40	> 125	1.2
1,6-Hexanediol	0.31	75-80	32	80	> 125	1.4
1,10-Decanediol	0.20	34-36	25	29	> 125	4.9
1,20-Eicosanediol	0.08	47-49	45	48	> 50	3.0
1,2-Propanediol	0.11	80-87	54	67	> 50	4.9
1,3-Butanediol	0.12	50-55	25	33	> 50	4.5
Diethylene glycol	0.20	55-60	24	30	> 125	3.3
Triethylene glycol	0.13	60-65	33	64	> 50	9.5

Evaluation of Experimental Results

The change of melting points of polyesters of terephthalic acid is plotted in Fig. 1 as a function of the number of carbon atoms in the molecule of polymethylene glycol. We see from Fig. 1 and the data of Table 1 that the melting points of esters with an even number of carbon atoms lie on a smooth curve. The melting point falls with increasing chain length of the glycol (256° for polyethylene terephthalate to 108° for the ester of eicosanediol).

The melting points of polyesters of terephthalic acid generally change in the same manner as those of fatty acids. Thus, the polyester of pentamethylene glycol melts lower than both of the even-membered neighboring polyesters (polytetramethylene terephthalate and polyhexamethylene terephthalate). Introduction of an ethereal linkage into the glycol molecule, as in the cases of polyesters of diethylene glycol and triethylene glycol, as well as of a lateral methyl group (polyesters of propylene glycol and 1,3-butanediol) lowers the melting point. Thus, polyesters of diethylene glycol and terephthalic acid melt at 65° and the polyester of propylene

TABLE 3

Properties of Polyesters of Phthalic Acid and Various Glycols

Name of glycol	Specific viscosity of 0.5% solution of polyester in crestol	Temperature in °C			Solubility of polyester in g/liter	
		of melting	of transition to viscofluid state	of fluidity	in benzene	in alcohol
Ethylene glycol	0.09	63-65	37	46	38.9	2.8
1,4-Butanediol	0.12	17-18	−14	14	> 50	16.0
1,5-Pentanediol	0.16	6-9	−19	5	> 50	2.6
1,6-Hexanediol	0.20	0-2	−14	2	> 50	2.1
1,10-Decanediol	0.10	−27- −26	−42	−29	> 50	9.7
1,20-Eicosanediol	0.10	47-52	—	—	—	—
1,2-Propanediol	0.13	45-50	33	42	> 50	10.5
1,3-Butanediol	0.12	−8-0	−19	−6		
Diethylene glycol	0.08	10-11	−25	7	> 50	8.0
Triethylene glycol	0.12	−8- −7	−28	−12	> 50	9.3

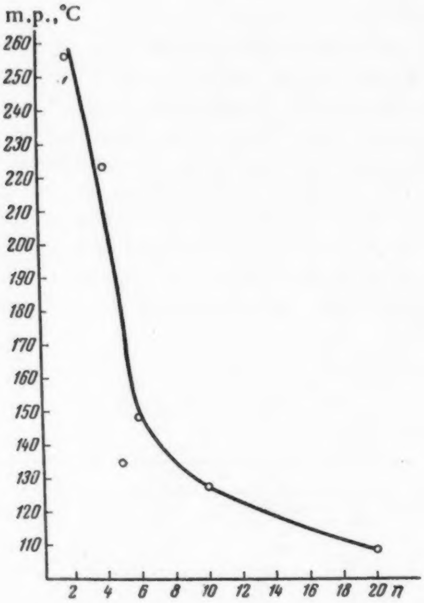


Fig. 1. Change of melting points of polyesters of terephthalic acid as a function of the number of carbon atoms in the molecule of polymethylene glycol.

glycol at 106°, whereas polyeicosamethylene terephthalate melts at 108° (lowest of the polyesters of the polymethylene glycol series). Polyesters of terephthalic acid are very poorly soluble in such solvents as benzene and ethyl alcohol. For example, the polyesters of ethylene glycol, tetramethylene glycol, hexamethylene glycol and decamethylene glycol are completely insoluble in ethyl alcohol and benzene. Introduction of an ethereal linkage and of a side methyl group into the glycol molecule increases the solubility of polyesters. Maximum solubility in benzene is exhibited by polyesters of terephthalic acid with propylene glycol and 1,3-butanediol, as well as with di- and triethylene glycols.

Changes of melting points of polyesters of isophthalic acid are plotted as a function of the number of carbon atoms in the molecule of polymethylene glycol in Fig. 2. This curve and the data of Table 2 show that the melting points pass through a minimum. The temperatures of transition of polyesters of isophthalic acid and polymethylene glycols into the viscoliquid state change in parallel with the melting points. Polydecamethylene isophthalate has the lowest temperature of transition into the viscoliquid state. It should be noted that the temperature of passage of the polyester of pentamethylene glycol into the viscoliquid state is slightly below those of the polyesters of the neighboring glycols (tetramethylene glycol and hexamethylene glycol), whereas the melting point of polypentamethylene isophthalate was slightly higher than the melting point of polyhexamethylene isophthalate. Polyesters of phthalic acid are very much more soluble in benzene than in alcohol.

In Fig. 3 is plotted the change of melting point of polyesters of phthalic acid and polymethylene glycols in dependence on the number of carbon atoms in the molecule of glycol; the diagram shows that with increasing length of the methylene chain in the original glycol from 2 (ethylene glycol) to 10 (decamethylene glycol)

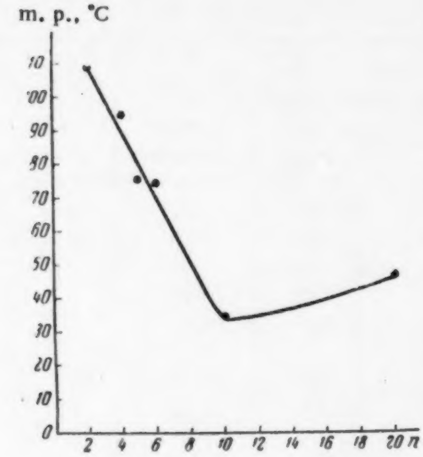


Fig. 2. Change of melting point of polyesters of isophthalic acid as a function of the number of carbon atoms in the molecule of polymethylene glycol (n).

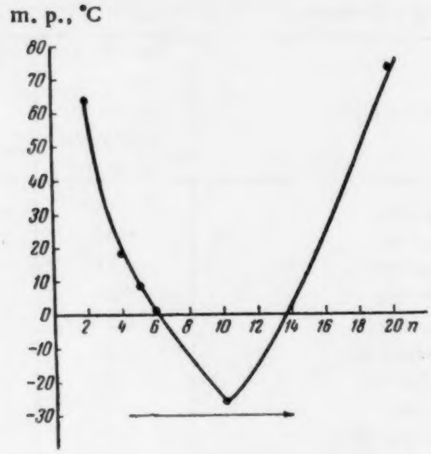


Fig. 3. Change of melting point of polyesters of phthalic acid in dependence on the number of carbon atoms in the molecule of polymethylene glycol (n).

the melting point of polyesters of phthalic acid changes from 63 to −27°; further increase in the number of methylene groups in the glycol up to 20 raises the melting point of the polyester; polyeicosamethylene phthalate melts at 47°. The trend of change of temperatures of passage into the viscoliquid state of polyesters of phthalic acid is similar in character to the changes of melting point; the polyester of decamethylene glycol has the lowest temperature of passage into the viscoliquid state. The temperature of transition into the viscoliquid state of polypentamethylene phthalate (−19°) is a little below the transition temperature of polyhexamethylene phthalate (−14°), i. e., it does not fit onto the curve of transition temperatures of the polyesters of even-numbered glycols. Comparison of the temperatures of transition into the viscoliquid state and into the liquid state of polyesters of phthalic acid reveals a considerable interval between them, which reaches 16° with the ester of hexamethylene glycol, 24° in the case of the ester of pentamethylene glycol, etc. This behavior points to a well-developed amorphous structure of these polymers.

TABLE 4

Melting Points of Some Esters of Isomeric Phthalic Acids

Ester	Acid		
	terephthalic	isophthalic	phthalic
Monomethyl	230	193	82.5
Monoethyl	165	115	2
Monopropyl	127	–	54
Monobutyl	122	–	73
Dimethyl	140	67	4
Diethyl	43	11.5	–
Dipropyl	31	–	–
Dibutyl	16	–	–
Dicetyl	–	–	42
Dimyricyl	–	–	79
Diphenyl	191	120	73
Dibenzyl	–	–	42

Introduction of an ethereal bond into a glycol molecule leads to an appreciable change in the properties of the resultant polyesters of phthalic acid. For example, polyesters of phthalic acid with diethylene glycol and triethylene glycol are liquids at the ordinary temperature, whereas polyethylene phthalate melts at 63°. Lowering of the melting point also follows the introduction into a glycol molecule of a lateral methyl group; for example, the polyester of 1,2-propanediol melts at 45°. Comparison of the properties of polyesters of terephthalic isophthalic and phthalic acids shows that they differ from one another considerably. Polyesters of terephthalic acid have the highest melting points, followed in order by the esters of isophthalic and phthalic acids. The majority of the polyesters of terephthalic acid and polymethylene glycols are crystalline substances, whereas among the corresponding polyesters of isophthalic and phthalic acids are rubber-like (e. g., polypentamethylene isophthalate and polytetramethylene phthalate) and even liquid substances (polydecamethylene phthalate and polyhexamethylene phthalate). Polyesters of terephthalic acid are very much less soluble in benzene and alcohol than the corresponding polyesters of isophthalic and phthalic acids.

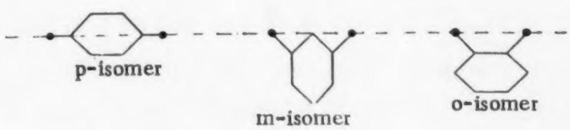
An understanding of the causes of the different properties in the various series of polyesters of terephthalic, isophthalic and phthalic acids calls for consideration of the structural features of the polymer chains of these polyesters. Polyesters of the phthalic acids differ from polyesters of aliphatic acids by containing, apart from $-CO-$, $-O-$, $-CH_2-$, and $-\underset{|}{C}H-$, also an aromatic ring. This aromatic ring, however, does not exert the same influence in the polyesters of terephthalic, isophthalic and phthalic acids. Taking as examples the low molecular esters of the isomeric phthalic acids, we see that the para-isomers have the highest melting points, followed

TABLE 5

Melting Points of Polyesters of Isomeric Phthalic Acids and of Esters of Adipic, Glutaric and Succinic Acids

Name of glycol	Acids					
	terephthalic	adipic	phthalic	glutaric	phthalic	succinic
Ethylene glycol	256	47	103	−19	63	102
Pentanediol-1,5	134	36	76	22	6	32
Hexanediol-1,6	148	55	75	28	0	52
Decanediol-1,10	123	70	34	55	−27	71
Eicosanediol-1,20	108	85	47	77	47	86
Propanediol-1,2	106	−25	80	−25	45	− 2
Butanediol-1,3	82	−36	50	−36	−8	−15
Diethylene glycol	65	−29	55	−30	10	−11
Triethylene glycol	60	−39	60	−36	−8	−24

in order by the meta- and the ortho-isomers. Some data for melting points of esters of isomeric phthalic acids are presented in Table 4. The difference in melting points both of the esters and polyesters of the phthalic acids is evidently associated with the different degrees of symmetry of their molecules and in turn with the degree of density of packing of the molecules in the crystal. Indeed, by representing the isomeric phthalic acids in the following manner:



we can see that maximum symmetry in relation to the axis is exhibited by terephthalic acid and the minimum by o-phthalic acid, i. e., esters and polyesters of terephthalic acid can have more densely packed polymeric chains and a more regular arrangement of the macromolecules, which is manifested in such properties as melting point, temperature of transition into the viscoliquid state, solubility, etc.

Comparison of the melting points of polyesters of terephthalic, isophthalic and phthalic acids with the melting points of the corresponding polyesters of aliphatic acids (adipic, glutaric, succinic) in Table 5 shows

that the melting points of polyesters of adipic acid are considerably below the melting points of the corresponding polyesters of terephthalic acid. Polyesters of succinic acid and polymethylene glycols melt higher than the corresponding polyesters of phthalic acid. Polyesters of isophthalic acid melt higher than polyesters of glutaric acid right up to the polyester of decamethylene glycol; from this point onwards the polyesters of glutaric acid have the higher melting points. Consequently, the introduction of an aromatic ring into a molecule of polyester is not always accompanied by increasing melting point of the polymer, but only in certain cases.

The higher melting points of polyesters of terephthalic acid in comparison with polyesters of adipic acid are associated with the greater symmetry of the macromolecule of polyethylene terephthalate in which there are 4 types of groups:  , $-CO-$, $-O-$, and $-CH_2-$. Evidently we are dealing with denser packing of the macromolecules caused either by stronger interaction between the chains due to the favorable conjunction of the carbonyl group with the benzene ring, or by the greater rigidity of the polymeric chain due to the presence in it of p-phenylene links. The higher melting points of the polyesters of succinic acid in comparison with the corresponding polyesters of phthalic acid may be attributed to the reduced closeness of packing due to the nonsymmetrical structure of phthalic acid itself. This may also account for the fact that the introduction into the molecule of polyester of succinic acid of a lateral methyl group (polyesters of propylene glycol and butanediol-1,3) leads to a sharper fall in melting point in comparison with the corresponding polyesters of phthalic acid, in which the closeness of the packing is already reduced. The fall in melting point of polyesters of terephthalic acid with increasing length of methylene chain in the glycol, characteristic also of the low-molecular esters (Table 4), is explained by the increased pliancy of the polymeric chain due to the fall in influence of its p-phenylene linkages.

In the polyesters of isophthalic and phthalic acids, the elimination of the effect of the aromatic ring and of the carbonyl group takes place more rapidly than in polyesters of terephthalic acid. This also accounts for the fact that starting from the polyester of decamethylene glycol we observe a rise in the melting points of the polyesters of these acids, which is due to the increased rigidity of the polymeric chain resulting from accumulation of methylene groups in the polymeric molecule. The lower melting points and lower temperatures of transition to the viscoliquid state of polyesters of isomeric phthalic acids with pentamethylene glycol do not represent an exception to the rule since a similar phenomenon is also observed in the polyesters of aliphatic dicarboxylic acids [7] and is associated with the presence of an odd number of methylene groups in the molecule of pentamethylene glycol.

SUMMARY

1. Syntheses were effected of polyesters of terephthalic, isophthalic and phthalic acids with various glycols of the general formula $HO(CH_2)_nOH$, as well as with diethylene glycol, triethylene glycol, propylene glycol and butanediol-1,3.

2. The problem of the influence of the structure of the starting substances on the properties of the resultant polyesters was discussed.

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HETEROCHAIN POLYESTERS

2. POLYESTERS OF ISOMERIC DIPHENYLDICARBOXYLIC ACIDS

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In the preceding communication [1], we considered the polyesters of the isomeric phthalic acids with various glycols. It was shown that the physical properties of these polyesters depend essentially both on the structure of the aromatic acid and on the structure of the aliphatic glycol. The higher melting points of polyesters of terephthalic acid in comparison with esters of isophthalic and phthalic acids was attributed to the high degree of symmetry of the molecules of polyesters of terephthalic acid. It was also emphasized that the presence of an aromatic ring in the polyester chain does not always result in a rise in melting point by comparison with aliphatic polyesters. Thus, for example, the polyesters of succinic acid melt higher than the corresponding polyesters of polymethylene glycols with phthalic acid, notwithstanding that the latter contain the residue of an aromatic dicarboxylic acid in their chain.

It was of interest to continue this investigation by studying polyesters of other aromatic dicarboxylic acids with the objective of obtaining a more detailed insight into the influence of the symmetry of the polymeric chain and of the presence of aromatic nuclei on the physical properties of polyesters. For this purpose we considered the most promising starting substances to be the polyesters of aromatic acids containing two aromatic rings, namely esters of diphenic acid, p,p'-diphenyldicarboxylic acid and m,m'-diphenyldicarboxylic acid. Esters of these acids with the following glycols were prepared: propylene glycol, butanediol-1,3, diethylene glycol, triethylene glycol, and glycols with the general formula $HO(CH_2)_nOH$, where n = 2 to 6, 8, 20. The majority of these polyesters were prepared and investigated here for the first time. Only brief mention is made in the literature about the polyesters of diphenic acid with ethylene and diethylene glycols [2]; also about the esters of p,p'-diphenyldicarboxylic acid with ethylene glycol [2-4], tetramethylene glycol [3], hexamethylene glycol [4] and diethylene glycol [2]. There is also a reference to the amorphous structure of the polyester of m,m'-diphenyldicarboxylic acid with ethylene glycol [4].

DISCUSSION OF RESULTS

In Table 1 are presented the data that we obtained in the investigation of polyesters of p,p'-diphenyldicarboxylic acid and aliphatic glycols of various structures. These results, together with the plots of changes of melting point of polyesters of glycols of the polymethylene series (Fig. 1), indicate that with growth of the methylene chain in the original even-membered glycol the melting points of the polyesters gradually decrease from 330° (polyester of ethylene glycol) to 112° (polyester of eicosamethylene glycol). Polyesters of odd-membered polymethylene glycols melt lower than the polyesters of the neighboring even-membered glycols. Thus, the melting point of the polyester of p,p'-diphenyldicarboxylic acid with trimethylene glycol is 246°, whereas the polyester of ethylene glycol melts at 330° and that of tetramethylene glycol at 255°. Change of structure of the original glycol (introduction of a lateral methyl group or an ethereal linkage) leads to considerable fall in melting point of the polyesters obtained from such glycols. Thus, the polyester of p,p'-diphenyldicarboxylic acid with propylene glycol melts at 130°, and that with diethylene glycol at 117°, whereas the ester with ethylene glycol melts at 330°, and that with pentamethylene glycol at 160°. A characteristic feature of polyesters of p,p'-diphenyldicarboxylic acid is their very poor solubility in such organic solvents as benzene and ethyl alcohol. Polyesters of the first even-membered polymethylene glycols are distinguished by exceptionally poor solubility (esters of ethylene glycol and tetramethylene glycol do not dissolve even in cresol).

TABLE 1

Polyesters of p,p'-Diphenyldicarboxylic Acid

Serial number	Name of glycol	Melting point in°C	Solubility in g/liter		Specific viscosity of 0.5% solution of polymer in crestol
			in alcohol	in benzene	
1	Ethylene glycol	330-333	0	0	–
2	Trimethylene glycol	246-249	–	–	0.13
3	Tetramethylene glycol	255-260	–	–	–
4	Pentamethylene glycol	160-170	0.9	3.3	0.15
5	Hexamethylene glycol	195-200	–	–	0.08
6	Decamethylene glycol	126-132	–	–	0.06
7	Eicosamethylene glycol	112-115	–	–	0.07
8	Diethylene glycol	117-119	2.3	5.5	0.05
9	Triethylene glycol	86-93	–	–	0.05
10	Propylene glycol	130-140	3.3	5.3	0.05
11	Butanediol-1,3	125-135	–	–	0.05

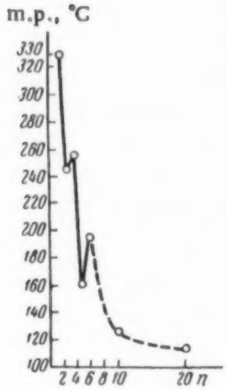


Fig. 1. Change of melting point of polyesters of p,p'-diphenyldicarboxylic acid in dependence on the number of carbon atoms (n) in the molecule of glycol.

On comparing the melting points of polyesters of m,m'-diphenyldicarboxylic acid and polymethylene glycols (Table 2), we can conclude that increase in the number of methylene groups in the original glycol to 6 is accompanied by a fall in melting point of the polyesters from 119° (ethylene glycol) to 52° (hexamethylene glycol). However, further increase in the number of methylene groups to 10 (in the case of the polyester of decamethylene glycol) and to 20 (polyester of eicosamethylene glycol) is accompanied by a rise of the melting point of the polyester in comparison with the polyester of hexamethylene glycol. A feature of the polyesters of m,m'-diphenyldicarboxylic acid is the absence of an "even-number" effect, i. e., the melting points of the polyesters of odd-numbered glycols are not lower than those of neighboring even-numbered members. Another characteristic is that change of structure of the glycol does not influence the properties to the same extent as in the case of polyesters of p,p'-diphenyldicarboxylic acid or of polyesters of aliphatic dicarboxylic acids. Change of the temperature of transition to the viscoliquid and liquid states in the case of polyesters of m,m'-diphenyldicarboxylic acid has a character similar to that of the change of melting points: the polyester of m,m'-diphenyldicarboxylic acid with hexamethylene glycol has the lowest transition temperature of all of the investigated polyesters of polymethylene glycols. The highest temperatures of transition are exhibited by polyesters of decamethylene glycol and eicosamethylene glycol. Another feature of these polyesters is that their solubility is lower between the temperatures of transition to the viscoliquid and liquid states. This fact indicates that they are less amorphous. Of all of the investigated polyesters of m,m'-diphenyldicarboxylic acid, only the polyesters of decamethylene glycol and eicosamethylene glycol were opaque substances.

Data for polyesters of diphenic acid are given in Table 3. They show that increase of the number of methylene groups in the original glycol leads to fall in the melting point of the polyesters. Thus, for example, the polyester of diphenic acid with ethylene glycol is a transparent solid with m. p. 96°, whereas the polyester of eicosamethylene glycol is a liquid with a melting point of −18°. The zigzag form of the curve of change of melting points of polyesters in dependence on the number of carbon atoms in the glycol is absent in the case of polyesters of diphenic acid, indicating that the "even-number" factor does not come into play for polyesters of this acid. Polyesters of diphenic acid with ethylene glycol, propylene glycol and diethylene glycol are readily soluble in

TABLE 2

Polyesters of m,m'-Diphenyldicarboxylic Acid

Serial number	Name of glycol	Temperature in °C			Solubility in g/liter		Specific viscosity of 0.5% solution of polymer in cresol
		of melting	of transition to the visco-liquid state	of fluidity	in alcohol	in benzene	
1	Ethylene glycol	119-122	–	100	0	2.0	0.109
2	Trimethylene glycol	76-78	49	67	–	–	0.04
3	Tetramethylene glycol	62-66	30	79	–	–	0.06
4	Pentamethylene glycol	57-60	30	42	–	16	0.086
5	Hexamethylene glycol	52-56	25	39	–	–	0.094
6	Decamethylene glycol	86-90	86	96	–	–	0.079
7	Eicosamethylene glycol	89-91	87	96	–	–	0.079
8	Diethylene glycol	69-75	42	63	1	44.5	0.11
9	Triethylene glycol	43-46	18	36	–	–	0.105
10	Propylene glycol	93-97	53	95	1.9	49.7	0.094
11	Butanediol-1,3	85-87	34	78	–	–	0.093

TABLE 3

Polyesters of Diphenic Acid

Serial number	Name of glycol	Temperature in °C			Solubility in g/liter		Specific viscosity of 0.5% solution of polymer in cresol
		of melting	of transition to the viscoliquid state	of fluidity	in alcohol	in benzene	
1	Ethylene glycol	96-98	50	88	1.6	> 50	0.10
2	Trimethylene glycol	70-78	47	60	–	–	0.08
3	Tetramethylene glycol	34-36	24	33	–	–	0.08
4	Pentamethylene glycol	8-13	−11	8	6.1	> 50	0.06
5	Hexamethylene glycol	4-9	–	–	–	–	0.08
6	Decamethylene glycol	−7- −3	–	–	–	–	0.10
7	Eicosamethylene glycol	−18- −16	–	–	–	–	0.08
8	Diethylene glycol	54-59	38	51	2.5	> 50	0.16
9	Triethylene glycol	38-41	17	33	–	–	0.16
10	Propylene glycol	51-55	24	36	25	> 50	0.04
11	Butanediol-1,3	36-38	24	35	–	–	0.06

benzene and very much less soluble in alcohol. Comparison between the polyesters of p,p'-diphenyldicarboxylic acid, m,m'-diphenyldicarboxylic acid and diphenic acid shows great differences between them. Whereas polyesters of p,p'-diphenyldicarboxylic acid are solid, opaque substances, the majority of the esters of m,m'-diphenyldicarboxylic acid are transparent, and some of the polyesters of diphenic acid are even liquid. Polyesters of p,p'-diphenyldicarboxylic acids have the highest melting points, followed in order by the polyesters of m,m'-diphenyldicarboxylic acid and those of diphenic acid. Polyesters of p,p'-diphenyldicarboxylic acid are the least soluble; those of diphenic acid have the highest solubility.

In the case of polyesters of p,p'-diphenyldicarboxylic acid the change of structure of the glycol is sharply reflected in the properties of the polymers. This effect is not so pronounced in the case of polyesters of the other two isomers.

Polyesters of symmetrical isomeric diaromatic acids thus conform to the law that was established from data for polyesters of the isomeric phthalic acids. The higher melting points and lower solubility of polyesters

TABLE 4

Melting Points of Polyesters of p,p'-Diphenyldicarboxylic (I), Terephthalic (II) and Sebacic (III) Acids

Name of glycol	Acid		
	(I)	(II)	(III)
Ethylene glycol	330	256	74
Trimethylene glycol	246	217	49
Tetramethylene glycol	255	222	64
Pentamethylene glycol	160	134	53
Hexamethylene glycol	195	148	65
Decamethylene glycol	126	123	71
Eicosamethylene glycol	112	108	87
Propylene glycol	130	106	—34
Butanediol-1,3	125	82	—44
Diethylene glycol	117	65	44
Triethylene glycol	86	60	28

TABLE 5

Melting Points of Polyesters of m,m'-Diphenyldicarboxylic (I), Isophthalic (II) and Suberic (III) Acids

Name of glycol	Acid		
	(I)	(II)	(III)
Ethylene glycol	119	103	63
Trimethylene glycol	76	92	44
Tetramethylene glycol	62	88	—
Pentamethylene glycol	58	76	43
Hexamethylene glycol	52	75	61
Decamethylene glycol	86	34	70
Eicosamethylene glycol	89	47	86
Propylene glycol	93	80	—41
Butanediol-1,3	85	50	—
Diethylene glycol	69	55	28

TABLE 6

Melting Points of Polyesters of Diphenic Acid (I), o-Phthalic (II) and Adipic (III) Acids

Name of glycol	Acid		
	(I)	(II)	(III)
Ethylene glycol	96	63	47
Trimethylene glycol	70	—	36
Tetramethylene glycol	34	17	57
Pentamethylene glycol	8	6	36
Hexamethylene glycol	4	0	55
Decamethylene glycol	— 7	—27	70
Eicosamethylene glycol	—18	47	85
Propylene glycol	51	45	—25
Butanediol-1,3	36	— 8	—36
Diethylene glycol	54	10	—29
Triethylene glycol	38	— 8	—39

of p,p'-diphenyldicarboxylic acid may be accounted for (as in the case of polyesters of terephthalic acid) by the greater degree of symmetry of the molecule of p,p'-diphenyldicarboxylic acid in relation to the m,m'- and o,o'-isomers. The influence of this greater degree of symmetry is manifested not only in the high melting points of polyesters of the p,p'-acid but also in the melting points of the low-molecular esters. For example, the dimethyl ester of p,p'-diphenyldicarboxylic acid melts at 214°, whereas the ester of the m,m'-acid melts at 102° and the ester of diphenic acid at 74°.

The disturbance of the closeness of packing of the polymer chains in the case of polyesters of diphenic and m,m'-diphenyldicarboxylic acids due to the lesser symmetry of their molecules in comparison with polyesters of p,p'-diphenyldicarboxylic acid is also reflected in the susceptibility of the polymers to crystallization. The majority of the investigated polyesters of diphenic and m,m'-diphenyldicarboxylic acids are transparent and amorphous; of 11 polyesters of m,m'-diphenyldicarboxylic acid only two are opaque (polyesters of decamethylene glycol and eicosamethylene glycol). A comparison was made of polyesters of isomeric phthalic and diphenyldicarboxlic acids on the one hand and of aliphatic dicarboxylic acids containing a number of carbon atoms equal to the number separating the carboxyl groups in the binuclear aromatic acids on the other hand. In this manner it was hoped to gain an insight into the influence of the aromatic rings upon the properties of polyesters. The melting points of polyesters of p,p'-diphenyldicarboxylic, terephthalic and sebacic acids are given in Table 4. It is seen that the introduction of a second aromatic ring into the molecule of an aromatic dicarboxylic acid leads to rise in the melting points of the polyesters. The maximum difference in melting points is exhibited by the polyesters of the first two aromatic acids with ethylene glycol, and amounts to 74°. With increasing size of the methylene chain in the original glycol, this difference decreases and in the long-chain polymethylene glycols (decamethylene glycol and eicosamethylene glycol) it is only 3°. The melting points of polyesters of sebacic acid are still lower than the melting points of the corresponding polyesters of p,p'-diphenyldicarboxylic acid. In this case, therefore, the replacement of the methylene chain of sebacic acid by an aromatic ring increases the melting point of polyesters, and the same effect results from increase of the number of aromatic nuclei.

Comparison of the melting points of polyesters of m,m'-diphenyldicarboxylic acid and isophthalic acid (see Table 5) shows that in spite of the presence of two aromatic rings in the molecule of m,m'-diphenyldicarboxylic acid, the melting points of its esters with tri-, tetra-, penta- and hexamethylene glycols are lower than the melting points of the corresponding polyesters of isophthalic acid. Just as in the preceding case, the melting points of polyesters of suberic acid are lower than those of m,m'-diphenyldicarboxylic acid with the exception of the polyester of suberic acid with hexamethylene glycol. Polyesters of suberic acid with deca- and eicosamethylene glycols melt higher than the corresponding polyesters of isophthalic acid. Polyesters of diphenic acid (Table 6), with exception of the polyester of eicosamethylene glycol, melt higher than the corresponding polyesters of phthalic acid. Comparison of the melting points of polyesters of diphenic acid and polymethylene glycols with the corresponding polyesters of adipic acid shows that replacement of the methylene chain of adipic acid by two aromatic rings leads to an increase in melting point of only the polyesters of the lower glycols (ethylene glycol and trimethylene glycol). The remaining polyesters of adipic acid melt higher than the corresponding esters of diphenic acid.

The foregoing facts permit us to conclude that replacement of the methylene groups of an aliphatic dicarboxylic acid by an aromatic nucleus does not always lead to rise of melting point of the polyester. Nor does an increase in the number of aromatic nuclei always have this effect. The polymeric chains of polyesters of aromatic dicarboxylic acids consist of various groups: $-CH_2-$, $-O-$, $-CO-$ and $-C_6H_4-$ which have different effects on the melting points of the compounds in question. We have previously made a close study of the influence of the $-CH_2-$, $-CO-$ and $-O-$ groups on the melting point of some aliphatic polyesters [5-7]. The aromatic nucleus plays a dual part in the polyester chain. In some cases its presence promotes a rise of melting point, while in others it has the opposite effect.

We can generalize our data for polyesters of isomeric aromatic acids with one and two rings in the molecule in the following manner: when the polyester is prepared from an aromatic dicarboxylic acid with a symmetrical structure, the aromatic ring in the polyester molecule promotes an increase in melting point relative to the corresponding polyester of the aliphatic dicarboxylic acid; the melting point of the polyester will increase with increasing number of aromatic rings in the molecule of acid.

The regularities of change of melting points in dependence on the structure of the glycol will be analogous to those in the series of polyesters of aliphatic dicarboxylic acids with the same number of carbon atoms between the carboxyl groups: polyesters of even-numbered glycols will melt higher than polyesters of the adjacent odd-numbered glycols; introduction of a lateral methyl group into the glycol molecule, also the introduction of an ethereal linkage, will appreciably lower the melting point of a polyester. A different picture is obtained when the polyester is prepared from an aromatic dicarboxylic acid whose carboxyl groups are not in the para- but in the ortho- or meta-position. In this case the mere presence of an aromatic ring in the polymeric change is not necessarily sufficient to give a polyester melting higher than the corresponding polyester of an aliphatic dicarboxylic acid. The melting points does not always rise even when the number of aromatic rings in the acid molecule is increased from one to two.

The fall of melting point of a polyester when an aromatic ring replaces the methylene groups in an aliphatic acid can be accounted for in this case by the decreased closeness of packing of the polymer chain due to the macromolecule becoming nonsymmetrical. The more nonsymmetrical the polymer chain, the lower the melting point of the polymer. Evidence of this is the lowering of the melting points of polyesters on passing from polyesters of terephthalic acid to polyesters of isophthalic acid and then to polyesters of phthalic acid; passage from polyesters of p,p'-diphenyldicarboxylic acid to polyesters of m,m'-diphenyldicarboxylic and diphenic acids is accompanied by the same effect. The great influence of the degree of symmetry of the polymeric chain is manifested in the fact that some polyesters of m,m'-diphenyldicarboxylic acid melt lower than the corresponding esters of isophthalic acid. Polyesters of m,m'-diphenyldicarboxylic acid are more symmetrical than polyesters of diphenic acid, although they are less symmetrical than polyesters of isophthalic acid. In the case of polyesters of m,m'-diphenyldicarboxylic acid we must take two factors into consideration in attempting to explain the change in melting points: 1) the increase in number of aromatic groups in the dicarboxylic acid molecule, which must raise the melting point (the dimethyl ester of isophthalic acid melts at 67°, but that of m,m'-diphenyldicarboxylic acid melts at 102°); 2) decreased symmetry of the macromolecule when compared with the polyester chain derived from isophthalic acid, which is bound to lead to a fall in melting point.

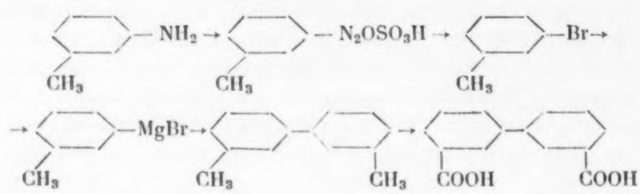
In the case of the polyester of m,m'-diphenyldicarboxylic acid with ethylene glycol, the first factor will predominate since the methylene chain in the original glycol is short and the effect of the aromatic ring in the polymeric chain will be proportionately weighty. Further increase in the number of carbon atoms in the glycol molecule leads to predominance of the second factor, and then greater weight attaches to the lower degree of symmetry of the molecule when compared with the plane, zigzag polymethylene chain. This explains why polyesters of m,m'-diphenyldicarboxylic acid with tri-, tetra-, penta- and hexamethylene glycols melt lower than the corresponding polyesters of isophthalic acid. In the case of polyesters of orthophthalic acid, the molecule is already so unsymmetrical that the introduction of a second aromatic ring has no appreciable influence on the change of closeness of packing of the polymeric chains. The predominating influence is then exercised by the concentration of aromatic rings, and this leads to a higher melting point in comparison with polyesters of phthalic acid. The influence of poor symmetry of the polymeric chain, which depends on the structure of the aromatic dicarboxylic acid with carboxyl groups in the ortho- and meta-positions, is predominant and is so large that the influence of modification of the structure of the glycol on the properties of the polyester is suppressed. When the even-number factor does not operate, the net result is a minute change of melting points of polyesters of glycols containing lateral methyl groups or ethereal linkages in comparison with polyesters of polymethylene glycols.

EXPERIMENTAL

Preparation of Starting Substances

1. Diphenic acid and its dimethyl ester. Diphenic acid was prepared from anthranilic acid by the method of Atkinson and Lawler [8]. The yield of diphenic acid was 72% of theory; m. p. 225-228° in agreement with the literature [8]. The dimethyl ester was prepared by esterification of the acid with methanol taken in 15-fold excess in presence of hydrogen chloride. An 80% yield of dimethyl ester was obtained; m. p. 73-74° in agreement with the literature [9].

2. m,m'- and p,p'-Diphenyldicarboxylic acids. Syntheses were effected according to the following scheme:



(the p,p'-isomer was similarly derived from p-toluidine).

a) m- and p-bromotoluenes. These were synthesized from m- and p-toluidines by the method of Bigelow [10] which was proposed for preparation of p-bromotoluene. Yield of m-bromotoluene 53-56% of theory; b. p. 49-51° (approximately 2-3 mm) or 184° at normal pressure (the literature gives 180-183° at 750 mm [11]). Yield of p-bromotoluene 77-82% of theory; b. p. 25-26° in agreement with the literature [10].

b) m,m'- and p,p'-ditolyls. Into a round-bottomed flask, fitted with reflux condenser and dropping funnel, were charged 12.9 g magnesium turnings and $^1/_3$ - $^1/_4$ part of a solution of 91 g m-bromotoluene in 240 ml absolute ether (the reaction was initiated by addition to the magnesium turnings beforehand of a crystal of iodine which was sublimed off; alternatively, 1-2 ml of methyl iodide was added after addition of $^1/_3$ of the ethereal solution). The remainder of the ethereal solution of m-bromotoluene was added dropwise in the course of the reaction. When the dropwise addition was completed, the reaction mass was heated for about 2 hours on a water bath. The resultant ethereal solution of organomagnesium compound was cautiously added dropwise, with stirring, to an ethereal solution of anhydrous copper chloride (72 g $CuCl_2$ in 240 ml ether) cooled to −6 to −12°. After completion of this operation, the reaction mixture was heated for an hour on a water bath, then cooled to room temperature and cautiously decomposed with water and diluted hydrochloric acid (1 : 1). The ethereal layer was separated, and washed with hydrochloric acid, ammonia and water. The ether was driven off, the residue was distilled in vacuum, and the fraction boiling at 118-120° at 2-3 mm or at 287° at normal pressure

was collected. According to the literature the b. p. is 286° at 716 mm [12]. Yield of m,m'-ditolyl 49.5% of theory. p,p'-Ditolyl was prepared from p-bromotoluene by the method of Sakellarios and Kyrimis [13]. It was purified by distillation in vacuum; b. p. 145° at 7 mm; yield about 50%; p,p'-ditolyl melted at 121° in agreement with the literature [14].

c) m,m'- and p,p'-diphenyldicarboxylic acids. These were obtained by oxidation of the corresponding ditolyls with potassium dichromate in a neutral medium in an autoclave under pressure (reaction temperature 275°, duration of reaction one hour):

$$CH_3C_6H_4C_6H_4CH_3 + 2K_2Cr_2O_7 + H_2SO_4 \rightarrow (C_6H_4COOK)_2 + K_2SO_4 + 2Cr_2O_3 + 4H_2O.$$

Yield of m,m'-diphenyldicarboxylic acid 62-67%, m. p. 345°. The literature gives m. p. 356° [15]. p,p'-Diphenyldicarboxylic acid was obtained in a yield of 80% of the theoretical.

d) Dimethyl ester of m,m'-diphenyldicarboxylic acid. The acid was esterified with methanol (10 g acid and about 200-300 ml of methanol) in presence of hydrogen chloride. The ester was purified by vacuum distillation, the fraction coming over at 205-210° (3-5 mm) being collected. Yield 73-80%; m. p. 102-103° in agreement with literature data [15].

e) Dimethyl ester of p,p'-diphenyldicarboxylic acid. Preparation was carried out via the acid chloride. A mixture of 47 g of the acid, 146 g of phosphorus pentachloride and 92 g of phosphorus oxychloride was refluxed for 20 hours. The phosphorus oxychloride was distilled off from the reaction mixture and the residual acid chloride was boiled for 20 hours with excess of methanol (700 ml). The dimethyl ester of p,p'-diphenyldicarboxylic acid came down on cooling the reaction mass. It was filtered and recrystallized from dichloroethane. Yield of ester about 65%; m. p. 213-214° in agreement with the literature [16].

3. Glycols. The glycols employed for preparation of polyesters were purified by distillation or by recrystallization, and their constants were in good agreement with the literature data.

Method of Preparation and Investigation of Polyesters

Polyesters of the isomeric o,o'-, m,m'- and p,p'-diphenyldicarboxylic acids were prepared by condensation of the corresponding dimethyl esters with glycols in presence of lithium hydroxide as catalyst. Polyesters of m,m'-diphenyldicarboxylic acid were obtained by the previously described procedure [6]. The conditions of condensation in the case of polyesters of diphenic acid and p,p'-diphenyldicarboxylic acids were the following: a) heating in a nitrogen stream; 2 hours at 170°, 10 hours at 180°, 2 hours at 190°, 2 hours at 200°, 0.5 hour at 220°, 1.5 hour at 250°; b) followed by heating in vacuum (approximately 2 mm) in a nitrogen stream for 1 hour at 190°, 2 hours at 200°, 2 hours at 210° and 7 hours at 220°.

The procedure was modified slightly in the preparation of polyesters of p,p'-diphenyldicarboxylic acid with ethylene glycol and butanediol-1,4. For preparation of the ethylene glycol ester the mixture, following heating in a nitrogen stream, was heated in vacuum at 355° for 15 minutes. In the case of the ester of tetramethylene glycol the vacuum heating was continued for 4 hours at 270°. The polyesters were investigated by the previously described procedure [17].

In conclusion the authors desire to express their gratitude to V. A. Zamyatina for kindly supplying them with the procedure for oxidation of p,p'-ditolyl.

SUMMARY

1. Polyesters of p,p'-diphenyldicarboxylic, m,m'-diphenyldicarboxylic and diphenic acids with aliphatic glycols were synthesized and investigated.

2. The problem of the influence of the structure of the starting substances on the properties of the polyesters was discussed.

3. The synthesis of m,m'- and p,p'-diphenyldicarboxylic acids was described.

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HETEROCHAIN POLYESTERS

3. POLYESTERS OF β-METHYLADIPIC AND β-(p-NITROPHENYL)-GLUTARIC ACIDS

V. V. Korshak and S. V. Vinogradova

In previous communications dealing with polyesters of propylene glycol [1] and butanediol-1,3 [2] we examined the influence of a lateral methyl group in the starting glycol on the properties of the polyester. It was of interest to clarify the action of a lateral substituent when it is not in the glycol residue but in the dicarboxylic acid residue. With this objective we synthesized and investigated polyesters of β-methyladipic and β-(p-nitrophenyl)-glutaric acid, i. e., acids in which one of the hydrogen atoms of a methylene group was substituted by a methyl or p-nitrophenyl group. We prepared and investigated polyesters of these acids by the previously described procedure [2, 3].

DISCUSSION OF RESULTS

Our results from a study of polyesters of β-methyladipic acid with a number of glycols are presented in Table 1. The glycols were those with the general formula $HO(CH_2)_nOH$ (n = 2-6, 10 and 20), also propylene glycol, butanediol-1,3, ethylene glycol and triethylene glycol. On comparing the change of melting point of

Polyesters of β-Methyladipic Acid*

Name of glycol	Temperature in °C			Solubility in g/liter		Mol. weight as determined from viscosity ($K = 0.93 \cdot 10^{-4}$ for benzene solution
	of melting	of transition to the visco-liquid state	of liquidity	in alcohol	in benzene	
Ethylene glycol	−31- −27	−46	−28	11.7	–	1200
Trimethylene glycol	−35- −31	below −56	–	17	–	1290
Tetramethylene glycol	−43- −38	below −60	−47	24.7	0.5 g in 5 ml	1030
"	−43- −38	–	–	9.9	–	4380
Pentamethylene glycol	−46- −42	below −60	−47	33	0.5 g in 5 ml	1200
"	−45- −40	"	−41	13.8	–	5000
"	−45- −41	"	–	16.2	–	3500
Hexamethylene glycol	−47- −42	below −50	−43	6.9	55.2	3700
Decamethylene glycol	− 3- − 2	2	8	4.3	0.5 g in 5 ml	5100
Eicosamethylene glycol	57-60	64	65	0.7	48.1	7100
Propylene glycol	−25- −21	below −40	−23	28.7	0.5 g in 5 ml	1940
Butanediol-1,3	−34- −30	−51	−37	51.5	The same	1840
Diethylene glycol	−29- −24	below −50	−32	16.7	"	1790
Triethylene glycol	−42- −38	below −58	−36	18.8	"	1730

* All the polyesters are liquids with the exception of the polyester of eicosamethylene glycol which is a white solid.

polyesters of the different polymethylene glycols in dependence on the number of methylene groups in the glycol, we see that the changes can be represented by a curve with a minimum corresponding to the polyester of β-methyladipic acid with hexamethylene glycol (m. p. −47°). Increase in the number of methylene groups in the glycol to 10 leads to rise of melting point of the polyester; polydecamethylene (β-methyladipate) melts at −3°. The polyester of eicosamethylene glycol is a solid melting at 57-60°. The melting points of the polyesters of tetramethylene glycol, pentamethylene glycol and hexamethylene glycol only differ slightly.

Data for the melting points of polyesters of adipic acid with various glycols are presented in Table 2. On comparing Tables 1 and 2 we see that the melting points of polyesters of β-methyladipic acid differ considerably from those of the corresponding esters of adipic acid. For example, all of the polyesters of adipic acid with

TABLE 2

Polyesters of Adipic Acid

Name of glycol	Melting point in °C	Solubility in alcohol in g/liter	Molecular weight
Ethylene glycol	47-52	11.5	2200
Trimethylene glycol	36-37	20.5	2100
Tetramethylene glycol	57-60	3.5	3920
Pentamethylene glycol	36-40	15.8	1880
Hexamethylene glycol	55-58	8.8	3080
Decamethylene glycol	70-74	–	3340
Eicosamethylene glycol	85-87	–	–
Propylene glycol	−25- −20	33.4	1130
Butanediol-1,3	−36- −34	–	1500
Diethylene glycol	−29- −24	11.3	3780
Triethylene glycol	−39- −30	20.6	2650

polymethylene glycols are solids, whereas the polyesters of β-methyladipic acid (excepting the polyester with eicosamethylene glycol) are liquids at the normal temperature. Another point that emerges is that the melting points of polyesters of adipic acid with odd-numbered glycols (e. g., trimethylene glycol and pentamethylene glycol) are lower than the melting points of the adjacent polyesters of even-numbered glycols. Consequently, the introduction of a side methyl group into the molecule of adipic acid in the β-position to the carboxyl leads to considerable change of properties of the polyesters of this acid. In the same way as a lateral methyl group in a glycol molecule (e. g., polyesters of propylene glycol), a lateral methyl group in adipic acid sharply depresses the melting points of the polyesters. On the other hand, a lateral methyl group in the dicarboxylic acid cancels out the even-number effect of the glycol. The very presence of a lateral methyl group in the polymeric chain evidently has a predominating influence in comparison with other factors.

Another interesting observation is that the change of structure of the glycol in the case of polyesters of β-methyladipic acid has no marked influence on the change of properties of these polyesters. Whereas in the case of polyesters of adipic acid the introduction of a side methyl group with an ethereal linkage into the glycol molecule sharply depresses the melting points of the polyesters (polyethylene adipate melts at 47°, polypropylene adipate melts at −25°, the polyester of diethylene glycol melts at −29°), introduction of the same groups into a glycol molecule in the case of polyesters of β-methyladipic acid is not accompanied by such a striking effect (the melting points of polyesters of β-methyladipic acid with propylene glycol and diethylene glycol are little different from the melting point of the polyester of ethylene glycol). Moreover, judging by the temperature of transition to the viscoliquid state, the introduction of an ethereal linkage into the glycol chain slightly increases the flexibility of the polyester chain, i. e, change of structure of the glycol is slightly reflected in the properties also in the case of polyesters of β-methyladipic acid.

It is necessary to point out that during the preparation of polyesters from β-methyladipic acid the polycondensation proceeded with very much greater difficulty in the case of some of the polyesters than in the case of adipic acid; the reaction is evidently hindered by the presence of the lateral methyl group. The consequence is that some of the polyesters prepared from β-methyladipic acid have a low molecular weight. We attempted

to obtain polyesters with slightly higher molecular weight by changing the conditions in some of the experiments (ratio of starting substances, catalyst). This was done, for example, in the case of polyesters of pentamethylene glycol and tetramethylene glycol. The melting points of the polymers, whose molecular weight differed from those obtained in the usual conditions by a factor of approximately four, only differed to an insignificant extent in comparison with polyesters of lower molecular weight. The temperatures of transition of polyesters of β-methyladipic acid into the viscoliquid state are fairly low.

Determination of the solubility of polyesters of β-methyladipic acid in ethyl alcohol and benzene showed that these polyesters are very much more soluble in benzene than in alcohol. Amounts of 0.5 g of the majority of the polyesters are fully soluble in 5 ml benzene; the poorest solubility in alcohol is exhibited by the polyester of β-methyladipic acid with eicosamethylene glycol (0.75 g/liter). In considering the solubility, however, we must not forget that the solubility of polyesters, unlike the melting points, is strongly dependent on the molecular weight of the polymer. Nevertheless, on comparing the solubilities in alcohol of the polyesters of ethylene glycol and trimethylene glycol, pentamethylene glycol and tetramethylene glycol, we can say that polyesters of odd-numbered glycols possess slightly better solubility than polyesters of neighboring even-numbered glycols (the molecular weights of these polyesters are of the same order). Comparison of the solubility in alcohol of the polyesters of β-methyladipic acid and adipic acid shows that the latter are rather more soluble.

TABLE 3

Polyesters of β-(p-Nitrophenyl)-glutaric and Glutaric Acids

Name of glycol	Temperature in °C				Molecular weight	Appearance
	of melting (glutaric acid)	β-(p-nitrophenyl)-glutaric acid				
		of melting	of transition to viscoliquid state	of liquidity	of polyesters of β-(p-nitrophenyl)-glutaric acid	
Ethylene glycol	−19-12	73-76	16	–	2300	Solid, transparent, colored
Pentamethylene glycol	22-25	–	9	37	3100	Rubbery
Hexamethylene glycol	28-34	–	19	38	5200	"
Eicosamethylene glycol	77-80	42-46	38	39	4900	Solid, colored

We prepared four esters of β-(p-nitrophenyl)-glutaric acid with ethylene glycol, pentamethylene glycol, hexamethylene glycol and eicosamethylene glycol. Data for these polyesters are given in Table 3 which shows that the introduction of the p-nitrophenyl group into glutaric acid in the β-position to the carboxyl leads to appreciable change of properties of the polyesters when compared with the corresponding polyesters of glutaric acid. Thus, the polyester of β-(p-nitrophenyl)-glutaric acid with ethylene glycol is a solid transparent substance melting at 73°, whereas polyethylene glutarate is a viscous liquid melting at −19°. Higher melting points are also found for the rubbery polyesters of β-(p-nitrophenyl)-glutaric acid with pentamethylene glycol and hexamethylene glycol in comparison with the corresponding polyesters of glutaric acid. The increase of melting points of the polyesters of β-(p-nitrophenyl)-glutaric acid in comparison with polyesters of glutaric acid may be attributed to the increased rigidity of the polymeric chain of the former polyesters due to the introduction of the strongly polar p-nitrophenyl group. On the other hand the depression of melting points of polyesters of β-(p-nitrophenyl)-glutaric acid with penta-, hexa- and eicosamethylene glycols in comparison with the polyester of ethylene glycol is evidently associated with weakening of the effect of the p-nitrophenyl group with increasing size of methylene chain in the original glycol, due to which the p-nitrophenyl group carries less weight in the polymethylene chain. On the basis of the data for the temperature of transition into the viscoliquid and liquid states, we can say that polyesters of β-(p-nitrophenyl)-glutaric acid with the first three glycols are highly amorphous, and this characteristic is weakened with increasing length of methylene chain in the original glycol (this is consistent with the decreasing difference between temperatures of transition into the viscoliquid and liquid states). The polyester of β-(p-nitrophenyl)-glutaric acid with eicosamethylene glycol is even crystalline.

On the basis of comparison of the data obtained for polyesters of β-methyladipic and β-(p-nitrophenyl)-glutaric acids, we can say that introduction of a side group into the molecule of the original dicarboxylic acid need not lead in all cases to a fall in melting point of its polyesters. The chemical nature of this lateral substituent must be taken into consideration.

SUMMARY

1. Polyesters of β-methyladipic and β-(p-nitrophenyl)-glutaric acids were synthesized and investigated.

2. The problem of the influence of the structure of the starting substances on the properties of their polyesters was discussed on the basis of the data obtained.

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THE SOLUBILITY OF CELLULOSE IN QUATERNARY AMMONIUM BASES

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Conflicting data have appeared in the literature on the question of the influence of structure and molecular weight of quaternary ammonium bases on the solubility of cellulose in them [1-4]. These discrepancies evidently resulted from the use by different authors of cellulose with varying degrees of degradation and varying reactivity. It is important to note that not one of the cited investigations gave the constants of the cellulose used in the work.

In connection with the study of the solubility of cellulose in quaternary ammonium bases it is also of interest to clarify the influence of caustic alkalies on the process. This aspect has not previously been touched upon in the literature. Only in one of the older patents [5] is it noted that in presence of sodium hydroxide the solubility of cellulose in quaternary bases is considerably improved.

In order to establish the influence of chemical structure of a base upon its solvent power for cellulose, we investigated one and the same cellulose preparation in different quaternary ammonium bases. The solubility of cellulose in one base (triethylbenzyl ammonium hydroxide) was also examined in presence of sodium, potassium and ammonium hydroxides. As the initial cellulosic material we used a viscose sulfite cellulose with a degree of polymerization of 860 and with a 91.2% content of α-cellulose. The degree of solubility of the cellulose was determined from the filterability index [6] of the solution. Following the criterion adopted for viscose solutions, solutions with good filtering properties are considered to be those with a filterability index of not more than 100 sec.

Results are presented in Tables 1 and 2.

The data show that only three of the investigated bases completely dissolve cellulose: dimethylphenylbenzylammonium, triethylbenzylammonium, and triethylfurylammonium hydroxides. These have a higher molecular weight than the hydroxides that only cause the cellulose to swell. Addition of sodium or potassium hydroxide to the solution of quaternary ammonium base markedly diminishes the solubility of cellulose; with more than 0.1% of alkali present in the solution, the cellulose only swells considerably with formation of a turbid mass; ammonium hydroxide in the solution in relatively large quantity does not influence the solubility of cellulose.

The authors [1-3] who indicated the possibility of complete solution of cellulose in tetraethyl-, trimethylphenyl- and trimethylbenzylammonium hydroxides evidently used a cellulose that had previously been subjected to drastic treatment. Products of degradation of cellulose are known to be highly soluble.

An interesting problem is the elucidation of the composition of the compound formed when cellulose reacts with a quaternary ammonium compound; also of interest is the modification resulting from addition of caustic alkalies. Applying the direct method of determination of the composition of alkali cellulose [7], we examined the compounds of cellulose with the bases mentioned. The cellulose chemically combined with organic and inorganic hydroxide was isolated from the solution or the swollen mass by means of isoamyl alcohol. The isolated compounds were examined for their molar ratio of cellulose to quaternary ammonium base or the ratio between cellulose, base and caustic alkali. Results are given in Table 3.

* Deceased.

TABLE 1

Dissolution of Cellulose in Various Quaternary Ammonium Bases

Serial number	Quaternary ammonium base	Molecular weight	Optimum conc. of base in %	Tempera-ture in °C	Viscosity of solution in sec	Filterability index in sec
1	$(CH_3)_2(C_6H_5)(C_6H_5CH_2)NOH$	229	38—42	20	270	20—40
2	$(C_2H_5)_3(C_6H_5CH_2)NOH$	209	32—34	20	250	20—35
3	$(C_2H_5)_3(C_4H_3OCH_2)NOH$	199	32—34	20	250	20—35
4	$(C_2H_5)_3(C_6H_5)NOH$	195	Aqueous solutions with concentrations of 25 to 50% at a temperature of 20 and −5° only cause swelling of the cellulose with formation of a turbid, unfiltrable mass			
5	$(CH_3)_3(C_6H_5CH_2)NOH$	168				
6	$(CH_3)_3(C_6H_5)NOH$	153				
7	$(C_2H_5)_4NOH$	147				

TABLE 2

Influence of Caustic Alkalies on the Solubility of Cellulose in Triethylbenzylammonium Hydroxide

Serial number	Content of caustic alkalies in solution in %			Filterability in sec	Viscosity in sec	Character of solution
	NaOH	KOH	NH_4OH			
1	—	—	—	20—35	230	Transparent
2	0.05	—	—	100—130	240	"
3	0.1	—	—	Infinity	250	"
4	0.2	—	—	"	450	Turbid mass
5	0.3	—	—	"	690	" "
6	1.0	—	—	"	1200	" "
7	—	0.05	—	46—70	250	Transparent
8	—	0.1	—	500	260	"
9	—	0.2	—	Infinity	390	Turbid mass
10	—	0.3	—	"	520	" "
11	—	1.0	—	"	1070	" "
12	—	—	0.1	26	247	Transparent
13	—	—	1.0	28	237	"
14	—	—	3.0	24	232	"
15	—	—	5.0	32	258	"

TABLE 3

Serial no.	Quaternary ammonium base	% composition of starting solution				Chemical composition of compound separated from solution
		cellu-lose	R_4NOH	NaOH	KOH	
1	$(CH_3)_3(C_6H_5CH_2)NOH$	3	34	—	—	$(C_6H_{10}O_5)_2 \cdot R_4NOH$
2	$(C_2H_5)_3(C_6H_5CH_2)NOH$	3	34	—	—	$(C_6H_{10}O_5)_2 \cdot R_4NOH$
3	$(C_2H_5)_3(C_6H_5CH_2)NOH$	3	34	0.5	—	$(C_6H_{10}O_5)_2 \cdot 0{,}6R_4NOH \cdot 0.5NaOH$
4	$(C_2H_5)_3(C_6H_5CH_2)NOH$	3	34	1.0	—	$(C_6H_{10}O_5)_2 \cdot 0{,}5R_4NOH \cdot 0.7NaOH$
5	$(C_2H_5)_3(C_6H_5CH_2)NOH$	3	34	—	0.5	$(C_6H_{10}O_5)_2 \cdot 0{,}8R_4NOH \cdot 0.3KOH$
6	$(C_2H_5)_3(C_6H_5CH_2)NOH$	3	34	—	1.0	$(C_6H_{10}O_5)_2 \cdot 0{,}7R_4NOH \cdot 0.4KOH$

These data show that interaction of cellulose both with a quaternary ammonium base that dissolves it completely and with a base that only swells it leads to a compound in which on the average one molecule of organic hydroxide is attached for every two glucose residues. The presence of sodium or potassium hydroxide in the solution leads to a decrease in the quantity of quaternary ammonium base chemically combined with the cellulose; in the latter case caustic alkali is combined together with the ammonium base.

A noteworthy feature of the results is the considerable binding by the cellulose of sodium and potassium hydroxides from solutions having low concentrations of these alkalies. The molar ratio between quaternary ammonium base and cellulose in the compound obtained by reacting cellulose with the given hydroxide approximately corresponds to the molar ratio between the sum of the hydroxides (ammonium base and sodium or potassium hydroxide) and the cellulose in the compound formed on dissolving the cellulose in the quaternary ammonium base in presence of caustic alkalies. In the latter case, however, the cellulose is completely insoluble and only swells strongly.

On the basis of the experimental results, the dissolving of cellulose in a quaternary ammonium base may be considered to proceed in the following manner: reaction of cellulose with the base causes solvation of the active cellulose groups by the polar groups of the solvent with formation of a chemical compound between cellulose and hydroxide; at the same time the nonpolar portion of the molecules of the base hinder reaction between the individual solvated cellulose chains; when the molecule of quaternary ammonium base is sufficiently large, the bonds between the cellulose macromolecules are completely broken, due to which the solvated cellulose chains pass into solution.

Quaternary ammonium bases that completely dissolve cellulose have a molecular weight (Table 1), and in turn a molecular volume, larger than that of hydroxides that only cause swelling of cellulose.

It may be suggested that when cellulose reacts with tetraethyl-, trimethylbenzyl- and trimethylphenylammonium hydroxides the size of the molecules of the latter is insufficient for complete prevention of reaction between the individual macromolecules of cellulose. In consequence cellulose does not dissolve in these hydroxides but only swells strongly. Addition to the investigated solution of sodium or potassium hydroxide leads to decrease in the number of molecules of quaternary ammonium base entering into reaction with the active cellulose groups, and creates the conditions for intensification of reaction between the individual macromolecules of cellulose. The consequence is reduced solubility of the cellulose.

The foregoing theory is supported by the fact that of the three inorganic caustic alkalies (NaOH, KOH, NH_4OH), ammonium hydroxide has no influence on the solubility of cellulose in organic bases, while the influence of potassium hydroxide is inferior to that of sodium hydroxide. As we know, ammonium hydroxide does not form a chemical compound with cellulose, while the energy of interaction of cellulose with sodium hydroxide is higher than the energy of interaction with potassium hydroxide.

SUMMARY

1. Cellulose is found to be completely soluble only in three bases: dimethylphenylbenzyl-, triethylbenzyl- and triethylfurylammonium hydroxides.

2. A mechanism for solution of cellulose in quaternary ammonium bases is put forward on the basis of the experimental data.

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BRIEF COMMUNICATIONS

FORMATION OF AMINO ACIDS IN WATER CONTAINING DISSOLVED CARBON DIOXIDE AND COLLOIDAL MOLYBDENUM OXIDE UNDER THE INFLUENCE OF ARTIFICIAL LIGHT

Krishna Bahadur and S. Ranganayaki

The action of light on an aqueous solution of paraformaldehyde containing ferric chloride and potassium nitrate leads to a series of reactions with formation of a small quantity of amino acids [1].

The nature of the acids formed depends both on the pH of the solution and on the duration of irradiation [2]. A possible reaction mechanism was also advanced for the formation of these amino acids [3]. It was observed that if a mixture of paraformaldehyde, molybdenum oxide and water was subjected to artificial illumination, a number of amino acids were likewise formed in the mixture. These observations were confirmed by Prof. L. Santamaria in the Milan Institute of General Chemistry [4] in work that will shortly be published. In these experiments the nitrogen entering into the composition of the amino acids comes from the air.

A similar fixation of nitrogen is observed to occur if the mixture contains a suitable catalyst such as molybdenum oxide in the colloidal form, if irradiation is applied to a previously sterilized aqueous mixture and if the solution contains a carbon source such as paraformaldehyde. In the experiments described in this communication, however, we established that if the water contains a certain quantity of dissolved carbon dioxide, then no other source of carbon is required. In our experiments the carbon of the synthesized amino acids is derived from dissolved carbon dioxide which on irradiation forms formaldehyde [5-7] from which are then obtained carbon-containing free radicals. The latter undergo a series of reactions activated and initiated by light and yield amino acids as the end product. Nitrogen is derived from the air.

EXPERIMENTAL

Colloidal molybdenum oxide was prepared by dissolving 10 g of potassium molybdate (free from amino acids) in 70 ml distilled water and adding 6N hydrochloric acid solution until the mixture was definitely acidic. The solution was placed in a parchment bag and dialyzed for 10 days with distilled water. Dialysis was performed in a 3-liter beaker into which was poured 2.5 liters of distilled water; the water was changed after each 24 hours. The so-prepared colloidal molybdenum oxide does not contain amino acids (analytical tests). Into each of two thoroughly cleaned 600 ml "Sigkol" beakers was poured 400 ml of twice-distilled water, and 20 ml of the colloidal solution prepared as above was added to each. Small quantities of these solutions were carefully withdrawn for analysis and found to be free from amino acids when analyzed.

Amino acids were determined by the method of radial paper chromatography as proposed by Giri [8-10], using Whatman No. 1 paper and a mixture of butanol, acetic acid and water as developing solution; an acetone solution of ninhydrin was used for coloring the zones. Each analysis was performed with 100 drops of solution on the filter paper.

The flasks containing the aqueous solutions were plugged with cotton wool and sterilized by heating for 30 minutes under a pressure of 0.7 kg/cm^2; then kept for 24 hours for the purpose of incubation. The flasks were then again sterilized as a precaution against possible previous inadequate sterility. After cooling, the flasks were placed for 24 hours in a carbon dioxide atmosphere to enable some of the gas to enter the solutions in the flasks.

One of the flasks was protected against the action of light by several layers of thick, black felt. Both of the flasks (one covered and the other unprotected against light) were placed at a distance of 45 cm from a 1000-watt electric lamp. The irradiation setup was located in a special chamber, the air in which was free from ammonia or volatile amines. The two flasks were put under the lamp simultaneously in order that both of the solutions (one uncovered, the other shielded against the light) should be at the same temperature.

The solutions were exposed to the lamp for 100 hours, after which the amino acids were investigated by the method described above.

No trace of amino acids was detected in the solution that had been kept in the dark. Traces of glycine, alanine, asparagic acid and norleucine were detected in the solution that had been exposed to the radiation.

DISCUSSION OF RESULTS

The exposure to light of an aqueous solution containing dissolved carbon dioxide and colloidal molybdenum oxide as catalyst results in activation of the carbon dioxide with formation of formaldehyde and free radicals; the latter then combine with atmospheric nitrogen to form amino acids. As already reported, formaldehyde is detected in the water containing dissolved carbon dioxide after irradiation [8-10].

SUMMARY

1. Irradiation of an aqueous solution of carbon dioxide containing colloidal molybdenum oxide as catalyst with the light of a 1000-watt electric lamp leads to synthesis in the solution of glycine, alanine, asparagic acid and norleucine. No amino acids were found in control experiments in the dark.

2. In this synthesis the carbon of the amino acids is derived from the carbon dioxide, and the nitrogen is directly fixed from the air.

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A METHOD OF QUANTITATIVE INVESTIGATION OF THE TAUTOMERIC KETO-CIS-TRANS-ENOLIC EQUILIBRIUM IN SOLUTIONS

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An equilibrium of three forms exists in the general case in solutions of β-dicarbonyl compounds with an open chain: ketonic, cis-enolic and trans-enolic. It is here assumed that the cis-form possesses an inner complex structure with an intramolecular hydrogen bond. In some cases (formylphenylacetic ester, etc.) the geometrical isomers of the enols have been isolated. Henecka [1] showed that some α- and γ-substituted β-dicarbonyl compounds do not give the known color reactions for the enolic forms with ferric chloride, although the bromometric titration results indicate that they contain a fair amount of enolic forms. He attributed this anomaly to the presence of only trans-enol forms (steric hindrance of cis-enolization) incapable of forming inner-complex salts.

If we regard keto-cis-trans-enol tautomeric equilibrium as a protolytic acid-base equilibrium, in which acids of three different chemical types participate, and if we apply the Brönsted-Izmailov theory [2], we can write the ionization constants of these acids in two selected solvents S_1 and S_2 in the following manner:

ketonic: $pK_{k.-S_1} = pK_{k.-S_2} + C_1$

cis-enolic: $pK_{c.e.-S_1} = pK_{c.e.-S_2} + C_2$

trans-enolic: $pK_{t.e.-S_1} = pK_{t.e.-S_2} + C_3$

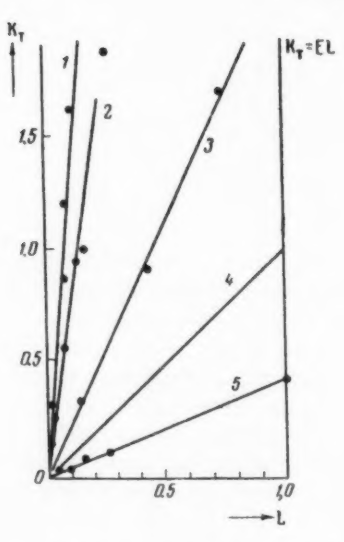

Fig. 1. K_T as a function of the solvent for: 1) cyclohexanonecarboxylic ester; 2) acetylcamphor; 3) benzoylacetic ester; 4) cyclopentanonecarboxylic ester.

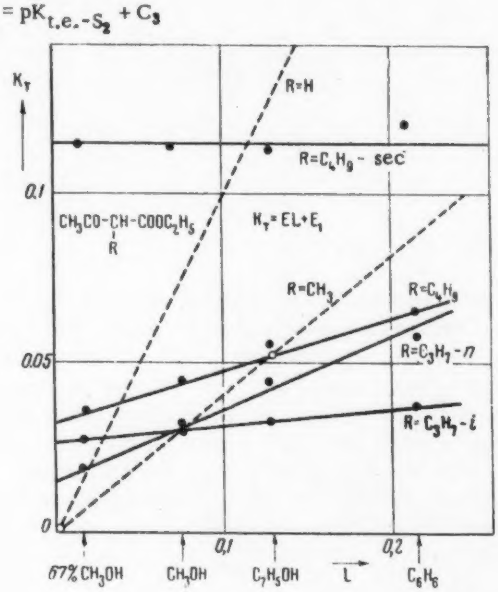

Fig. 2. K_T as a function of the solvent for α-substituted acetoacetic esters.

On then applying the chain of reasoning that we previously employed [3] in considering the chief laws of keto-enol equilibrium, we can derive an expression characterizing the change of constant of the ketone — total enols equilibrium with change of solvent:

$$K_{TS} = EL + E'L' \tag{1}$$

Here E and E' are the "enolizabilities" of the ketone forms in the direction of the cis- and trans-enolic forms, respectively, while L and L' are the "enolizing abilities of the solvent" (in cis- and trans-enolization). E and E' are independent of the solvent and are governed by keto-enol structure, while L and L' depend solely on the solvent; they are common to all keto-enols and are equal to the constants of the tautomeric equilibrium of the substances used as standards in cis- and trans-enolization. In the absence of trans-enolization E' = 0 and Eq. (1) is transformed into the known Meyer formula.

TABLE 1

Number of substance	Equilibrium constants				
	67% CH_3OH	CH_3OH	$CHCl_3$	C_2H_5OH	C_6H_6
I	24.4	28.1	24.4	24.6	Insoluble
II	—	1.26	1.55	1.58	1.43
III	—	2.51	2.74	2.78	2.55
IV	22.0	28.7	—	15.0	—

TABLE 2

R	E	E_1	% content of cis-enol in the enolic fraction			
			67% CH_3OH	CH_3OH	C_2H_5OH	C_6H_6
CH_3	0.4	0	Solely cis-form			
C_3H_7	0.201	0.015	25.1	51.1	63.4	75.0
C_4H_9	0.156	0.033	10.6	26.9	37.9	51.5
i-C_3H_7	0.050	0.026	4.6	13.0	19.9	30.1
sec.-C_4H_9	0.019	0.116	0.4	1.3	2.1	3.5

We determined the equilibrium position of a series of keto-enols in 67% methanol, methanol, ethanol, benzene and some other solvents by the bromometric method, using direct and back titration. We found that cyclopentanone-, cyclohexanone- and methylcyclohexanonecarboxylic esters, which are susceptible only to cis-enolization ("cis-fixed enols"), strictly follow the Meyer formula exactly like the other previously studied keto-enols with an open chain, as well as acetylcamphor for which cis-enolization is extremely probable. We see from Fig. 1 that the plots of K_T versus L for all these substances conform to the linear Meyer relationship (the straight lines pass through the origin). For ethyltetronic acid (I), the cyclic isopropylidene esters of methyl- and ethylmalonic acids (II) and (III) and 2-methyldihydroresorcinol (IV), for which only trans-enolization is possible (trans-fixed enols [4] but with once-occurring enolization), the equilibrium constant does not depend upon the solvent (Table 1).

It follows from these two series of experiments that, firstly, ethyl acetoacetate (Meyer's standard substance) can be retained as standard in cis-enolization, and, secondly, L' is a constant. Hence in place of Formula (1) we can write:

$$K_{TS} = EL + E_1. \tag{2}$$

Keto-enols, whose solutions contain both cis- and trans-enolic forms, should also be characterized by a linear relation between K_T and L, but the straight lines do not pass through the origin but intersect the ordinate at E_1. To this type must belong the keto-enols studied by Henecka, formylphenylacetic ester, etc. Results of determinations of K_T for α-alkylacetoacetic esters in the same solvents are plotted in Fig. 2. Whereas methylacetoacetic ester gives a straight-line plot passing through the origin (solely cis-enolization), propylacetoacetic ester cuts the ordinate at E_1, an indication of the presence of the trans-enolic form. Increasing branching of the chain of the substituent is accompanied by decrease of the tangent of the angle of slope (E) and the most sterically hindered sec.-butylacetoacetic ester corresponds to a straight line nearly parallel to the abscissa, which points to extremely slight cis-enolization and the approximation of this substance to the "trans-fixed" enols. From the data of Fig. 2 we calculated the content of cis-enolic forms in the enolic fraction of these keto-enols from the simple formula:

$$\text{cis-enol content} = \frac{100EL}{EL+E_1}\,\%. \tag{3}$$

Results are presented in Table 2 (R is the α-substituent).

In a similar manner we determined the cis-enol content in the enolic fraction of formylphenylacetic ester in various solvents. We found E = 7.253 and E_1 = 1.208. Hence, the content of cis-enol in the enolic fraction is 35.3% in $CHCl_3$, 57.3% in C_6H_6, 71.1% in ether and 87.7% in hexane. Consequently, the application of the theory of the acid-base tautomeric equilibrium permits quantitative evaluation of the content of the individual forms in solutions in the complex system ketone–cis-enol–trans-enol.

SUMMARY

1. The possibility of application of the fundamental laws of the acid-base protolytic equilibrium to the tautomeric equilibrium of a complex system containing ketonic and cis-trans-enolic forms is demonstrated.

2. A general formula is derived for determination of the tautomeric keto-cis-trans-enolic equilibrium constant. The known empirical formula of Meyer is a special case of this general law.

3. On the basis of data for α-substituted acetoacetic esters and for formylphenylacetic ester, a method is developed for quantitative determination of the content of cis-trans-enolic forms in solutions.

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METHODS OF PRODUCTION OF STRONGLY SCINTILLATING PLASTIC MASSES

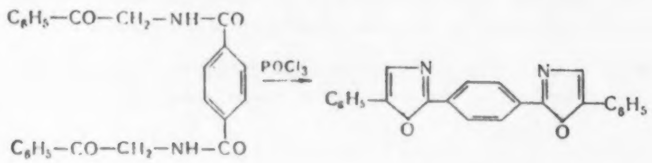
2. PREPARATION OF 1,4-DI-[2-(5-PHENYLOXAZOLYL)]BENZENE AND THE STUDY OF ITS SCINTILLATING EFFICIENCY IN POLYSTRYENE PLASTIC MASSES

N. A. Adrova and M. M. Koton

Much use has recently been made of scintillation counters (for recording radioactive radiations) on the basis of 1,4-di-[2-(5-phenyloxazolyl)]benzene both in solutions of aromatic hydrocarbons and in polystyrene as additive to the principal scintillator (p-terphenyl or 2,5-diphenyloxazole).

EXPERIMENTAL

For the synthesis of 1,4-di-[2-(5-phenyloxazolyl)]benzene we employed a method described by Hayes and co-workers [1]. The starting substance was phenacylamine hydrochloride which was transformed into diphenylacylterephthalamide. The latter was cyclized by heating with phosphorus oxychloride to form 1,4-di-[2-(5-phenyloxazolyl)]benzene according to the scheme:



Phenacylamine hydrochloride [2, 3] was prepared from ω-bromoacetophenone. The addition product of the latter with urotropine was formed and this was subjected to acid hydrolysis. To a solution of 8 g of terephthalyl chloride in 100 ml dry pyridine with stirring was added 14 g of phenacylamine hydrochloride, after which the reaction mixture was boiled for 15 minutes on a sand bath. After cooling, the contents of the flask were poured into water, and the precipitate was suction-filtered and dried. The yield of unpurified product was quantitative. The diphenacylterephthalamide was used for the next part of the synthesis without further purification.

A mixture of 4 g of diphenacylterephthalamide and 150 ml phosphorus oxychloride was boiled for 6-8 hrs. The greater part of the phosphorus oxychloride was then distilled off and the residue was run into water. The resultant crystals were suction-filtered and dried in the air. The product was purified by 2-3 recrystallizations from pyridine in presence of active charcoal, and it was chromatogrammed over alumina in toluene. The 1,4-di-[2-(5-phenyloxazolyl)]benzene obtained has m. p. 242-243°. The literature gives m. p. 237-238° [1], 245° [4]. Yield 39% reckoned on the diphenacylterephthalamide.

Scintillating plastic masses were prepared in the usual manner [3] but with the modification that the p-terphenyl and 1,4-di-[2-(5-phenyloxazolyl)]benzene incorporated in the monomeric styrene were dissolved by heating. The specimens were subjected to annealing for elimination of internal stresses. Efficient scintillating plastic masses were obtained by introducing 1,4-di-[2-(5-phenyloxazolyl)]benzene into polystyrene both in the capacity of the main scintillator (Table 1) and in the capacity of a supplement to the main scintillator (p-terphenyl, 2,5-diphenyloxazole) (Table 2).

TABLE 1

Scintillating Properties of a Plastic Mass Containing 1,4-Di-[2-(5-phenyloxazolyl)]benzene as the Main Scintillator

Serial number	Scintillating substance	Content of styrene (%)	Relative strength of impulses	Remarks
1	Terphenyl	2	100	
2	1,4-Di-[2-(5-phenyloxazolyl)]-benzene	0.5	102	
3	1,4-Di-[2-(5-phenyloxazolyl)]-benzene	1.0	90	Substance did not dissolve completely

TABLE 2

Influence of Addition of 1,4-Di-[2-(5-phenyloxazolyl)]benzene on the Scintillating Properties of Polystyrene Plastic Masses Containing p-Terphenyl and 2,5-Diphenyloxazole as the Chief Scintillator

Serial number	Content of scintillating substances in polystyrene in %			Relative strength of impulses
	p-terphenyl	2,5-diphenyl-oxazole	1,4-di-[2-(5-phenyl-oxazolyl)]-benzene	
1	2	—	—	100
2	2	—	0.01	132
3	2	—	0.02	139
4	2	—	0.05	128
5	2	—	0.1	123
6	—	1	—	105—115
7	—	1	0.01	100
8	—	1	0.02	115
9	—	1	0.05	117
10	—	1	0.1	117

We see from Table 1 that 1,4-di-[2-(5-phenyloxazolyl)]benzene possesses much higher activity in polystyrene than p-terphenyl; it was impossible, however, to introduce more than 0.5% of it into styrene due to its poor solubility, and this limits its application as scintillator. 1,4-Di-[2-(5-phenyloxazolyl)]benzene proved to be a very efficient additive to p-terphenyl when compared with diphenyloxazole (Table 2).

The enhanced scintillating efficiency of plastic masses containing a proportion of 1,4-di-[2-(5-phenyloxazolyl)]benzene can evidently be attributed to the shift of the maximum of the absorption and fluorescence spectra into the region of greater sensitivity of the photoelectric multiplier tube (FEU-19).

SUMMARY

1. 1,4-Di-[2-(5-phenyloxazolyl)]benzene was prepared in high purity.

2. A method of production of highly active plastic masses containing 1,4-di-[2-(5-phenyloxazolyl)]benzene and terphenyl was described.

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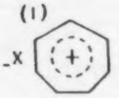
THE REACTION OF TROPILIDENE BROMIDE WITH PHOSPHORUS PENTACHLORIDE

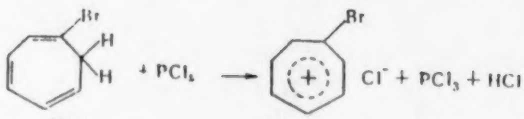
M. E. Volpin, I. S. Akhrem and D. N. Kursanov

In recent years the chemistry of the stable aromatic tropylium ion (I) [1] and of its derivatives has been developed.

(I)

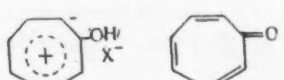


In the present work the method that we previously described [2] for preparation of tropylium salts by the action of PCl_5 on tropilidene was extended to tropilidene bromide (II, the position of the bromine is shown arbitrarily) with the objective of obtaining bromotropylium salts (III) according to the scheme:



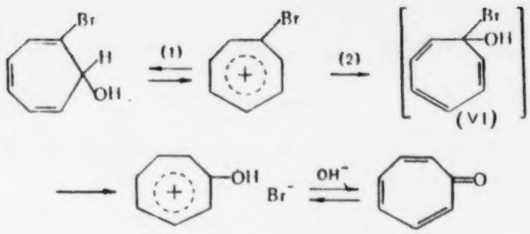
(II) (III)

It was found, however, that the product of reaction, when dissolved in water, does not form a solution of the bromotropylium salt (III) but is transformed into a tropylium hydroxide salt (IV) which is separated in the form of the chloroplatinate and by precipitation with tetraphenylboron-sodium. Neutralization of the tropylium hydroxide salt with sodium carbonate gives tropone (V), which has been described by Dauben and Ringold [3] and by Doering and Detert [4]. Tropone in turn is readily transformed into hydroxytropylium bromide (IV) (X = Br) by treatment with HBr:



(IV) (V)

This exchange reaction in which the poorly mobile bromine in tropylium bromide is replaced by hydroxyl is an unexpected one at first sight; it becomes understandable if we assume that the tropylium ions and the ions of its derivatives are present in water in an acid-base equilibrium [1]: $C_7H_7^+ + 2H_2O \rightleftarrows H_3O^+ + C_7H_7OH$. In the case of tropylium bromide the attack of the water molecule (or the OH^- anion) can take place either at one of the six unsubstituted carbon atoms or at the carbon atom linked to bromine. In the former case the reversible reaction (1) will take place; in the latter case (2) the product of addition (VI) will irreversibly split off the more



electrophilic Br atom (in the form of Br^-) with formation of tropylium hydroxide (in an acid medium) or tropone (with loss of HBr at higher pH values). Consequently, the whole of the tropylium bromide is substantially irreversibly transformed into tropylium hydroxide. It is likewise possible that the intermediate compound (VI) is not actually formed but that replacement of Br by OH proceeds by a S_N2 mechanism via the corresponding transition state. We can find an analogy to this type of facile nucleophile replacement of halogen in aromatic systems in the reactions of picryl chloride where the lability of the halogen is likewise induced by the ease of nucleophilic attack at the carbon atom linked to the halogen.

In a recent review [5] Doering points out that, according to his unpublished data, by bromination of tropilidene bromide and subsequent cleavage of HBr he obtained bromotropylium bromide which readily hydrolyzes to tropone. Our results are therefore in full accord with those of Doering.

EXPERIMENTAL

Tropilidene bromide. A solution of diazomethane (0.11 mole) in 4 liters of bromobenzene was exposed to ultraviolet irradiation until nitrogen ceased to come off. A fraction 9.59 g was isolated that had b. p. 48-81° (17 mm) and n_D^{20} 1.5670; it contained 69.4% of tropilidene bromide as determined by hydrogenation in alcohol over Pt-black. Yield of tropilidene bromide 35.4%.

Tropone. 0.53 g of tropilidene bromide and 1.32 g of PCl_5 were mixed in 10 ml anhydrous CCl_4 at room temperature for 5 hours. The precipitate was collected by filtration and dissolved in a small quantity of water. The aqueous solution was neutralized with sodium carbonate, extracted with ether and dried over sodium sulfate. Distillation of the solvent in vacuo left 0.21 g of a heavy, viscous liquid with b. p. 105° (10 mm); n_D^{25} 1.6095. The substance was identified as tropone (yield 63.7%). Literature data: b. p. 104-105.5° (10 mm); n_D^{25} 1.6090 [3].

Hydroxytropylium bromide. A benzene solution of tropone, prepared from 0.54 g tropilidene bromide and 1.31 g PCl_5, was saturated with HBr. 0.16 g of a white, nonhygroscopic substance came down, readily soluble in water and alcohol, insoluble in ether. On heating to 250° the substance charred without melting.

Found%: C 44.30, 44.59; H 3.91, 3.71; Br 42.57, 42.62. C_7H_7OBr. Calculated %: C 44.95; H 3.69; Br 42.72.

The whole of the bromine in the prepared substance is ionic, as was proved by titration with mercuric nitrate solution. Found 42.2% Br. Calculated for C_7H_7OBr 42.7%. The substance obtained is hydroxytropylium bromide. Ultraviolet spectrum of hydroxytropylium bromide in aqueous solution: λ_{max} = 312 mμ; log ϵ = = 3.96; the spectrum does not alter when the solution is acidified.

Tetraphenylboron-tropylium hydroxide. A solution of 0.15 g of tropilidene bromide in 2 ml heptane was boiled with 0.37 g of PCl_5 for 45 minutes with stirring. The precipitate was separated and dissolved in a small quantity of water. Addition of an aqueous solution of tetraphenylboron-sodium caused instantaneous precipitation of yellow tetraphenylboron-tropylium hydroxide. Yield 0.21 g (56.8%). The compound dissolves in alcohol; it is insoluble in water; it rapidly breaks down when stored.

Tropylium hydroxide hexachloroplatinate. 0.37 g of tropilidene bromide and 0.75 g of PCl_5 were boiled in heptane for 30 minutes while stirring. The precipitate was dissolved in dry nitromethane. The orange hexachloroplatinate was brought down from nitromethane on adding a concentrated aqueous solution of H_2PtCl_6. It

is insoluble in nonpolar solvents, soluble in alcohol and water. Tropylium hydroxide hexachloroplatinate was also obtained by treating tropone with a concentrated aqueous solution of H_2PtCl_6.

Found %: C 26.85, 26.94; H 2.60, 2.40. $C_{14}H_{14}O_2PtCl_6$. Calculated %: C 27.00; H 2.16.

SUMMARY

1. The action of PCl_5 on tropilidene bromide followed by treatment with water gives the hydroxytropylium salt which changes to tropone in alkali solution.

2. The data point to the ability of the bromine atom in bromotropylium salts to enter with facility into nucleophilic substitution reactions.

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LETTERS TO THE EDITOR

Dear Editor:

As we know from the literature, a number of attempts have been made to synthesize methylolpyrrolidone $(CH_2)_3CONCH_2OH$ (I). Reppe [1] reacted pyrrolidone with a 30% aqueous solution of formaldehyde in an acid medium and obtained a product to which he assigned the structure of (I). Breitenbach [2] later showed that the compound obtained by Reppe is $CH_2[N(CH_2)_3CO]_2$ (II), and not (I). Breitenback was also unable, however, to prepare (I).

The present writers prepared compound (I) in a study of the reaction of formaldehyde with lactams in an alkaline medium. By heating the reactants at 80-85° for 4-5 hours, the compound was obtained in 85-90% yield; m. p. 77-79.5°.

Found %: C 52.48, 52.39; H 7.75, 7.86; N 12.34, 12.26. $C_5H_9O_2N$. Calculated %: C 52.22; H 7.83; N 12.15. Hydroxyl number found: 460 . Hydroxyl number calculated: 487.

The structure of (I) was confirmed by its conversion into chloromethylpyrrolidone $(CH_2)_3CONCH_2Cl$ (III) by reaction with $SOCl_2$; yield 85%; b. p.97 -97.5° (4 mm); n_D^{20} 1.5022; d_4^{20} 1.2381; found MR 31.86; calculated for C_5H_8ONCl MR 31.90. Like the α-chloroethers, compound (III) is readily hydrolyzed by water with quantitative liberation of HCl; titration of the latter with 0.1 N NaOH solution indicated a molecular weight of 134.4 for (III); calculated molecular weight 133.6.

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Dear Editor:

FORMATION OF LiO_2 FROM $Li_2O_2 \cdot 2H_2O_2$

The ability to form superoxides, i. e., compounds whose crystal lattice consists of metal ions and molecular O_2^- ions, is characteristic of K, Rb, Cs and Na. The possible existence of the analogous lithium compound was postulated [1] only on the basis of evaluation of the absorption spectra of solutions of metallic lithium in liquid ammonia which were subjected to rapid oxidation with hydrogen at −78°. The synthesis of the compound $Li_2O_2 \cdot 2H_2O_2$ by Dobrynina [2] has enabled the present writers to give a more concrete proof of the existence of LiO_2. As was shown for $CaO_2 \cdot 2H_2O_2$ and $SrO_2 \cdot 2H_2O_2$ [3-4], the process of decomposition of peroxyhydrates of

peroxides leads under specific conditions to formation of a certain proportion of metal superoxide. We subjected the peroxyhydrate of lithium peroxide to drying in a vacuum-drying cupboard at a residual pressure of 10 mm mercury and at 100° (close to the temperature of decomposition of the H_2O_2 of crystallization in the compound $Li_2O_2 \cdot 2H_2O_2$) and so obtained for the first time a preparation containing about 9 wt.% LiO_2 in addition to Li_2O_2 and some LiOH and Li_2CO_3.

I. I. Volnov and A. N. Shatunina

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